



**Naval Surface Warfare Center
Carderock Division**
West Bethesda, MD 20817-5700

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Survivability, Structures, and Materials Directorate
Technical Report

**Chemistry and Properties of Slags from Navy Solid
Waste Destruction in the Plasma Arc System**

by

Inna G. Talmi, James A. Zaykoski and Curtis A. Martin

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13. ABSTRACT (Maximum 200 words) The U.S. Navy is currently developing a highly efficient shipboard system which employs a plasma torch to process Navy solid wastes primarily consisting of cardboard, paper, steel, aluminum, glass, and food waste. The objective of this research was to experimentally determine the melting behavior and properties of the slags resulting from the waste stream containing all five components, as well as various excursions. This study also investigated the corrosion resistance of various classes of refractories to resulting slags. A severe thermite reaction was observed in the "zero glass" excursion of the waste stream at about 1200 degrees C as a result of the chemical interaction between iron oxides and aluminum. This suggests the critical importance of the presence of a glass melt for suppression of the reaction. At least 50% of the glass as contained in the nominal waste stream is required to prevent the thermite reaction. In the absence of glass, the thermite reaction was suppressed by the introduction of the sand/soda mixture and sodium silicates with various SiO ₂ /Na ₂ O ratios or by sodium/potassium feldspar. The amount of flux required to suppress the thermite reaction depends on flux chemical composition, melting temperature, and viscosity.			
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Introduction

The U.S. Navy is currently developing a highly efficient shipboard Plasma Arc Waste Destruction System (PAWDS)¹ which employs a plasma torch to process Navy solid wastes primarily consisting of cardboard, paper, steel, aluminum, glass, and food waste. The products of this processing will be carbon dioxide and water (released as gases), and a slag composed of residual inorganic compounds. The composition, melting behavior, and properties of slags will depend on the composition of the waste stream and processing temperature and atmosphere. Because of shipboard size and weight limitations, the design of existing land-based incinerators (including commercial plasma reactors) cannot be adopted by the Navy.

To minimize ship impact, air, oxygen enriched air, and steam are the primary candidates for the torch gas. The oxidizing environment created in the reactor will lead to the oxidation of the metallic components of the waste stream. These oxides will combine with glass and the residual mineral constituents of paper and food forming a molten slag.

The overall objective of this research is the determination of the corrosion resistance of various classes of refractories to resulting slags, so that refractories offering the highest potential of long-term performance in contact with slags and gaseous atmosphere could be selected. The objective of the research documented in this report was to conduct laboratory modeling experiments to determine the melting behavior and properties of the slags resulting from the waste stream containing all five components (*nominal* slag), as well as the properties of slags resulting from various waste stream excursions designated as Zero Steel, Zero Glass, Zero Paper, or Zero Aluminum. These excursions were selected because of the inevitable variations in the composition of the waste stream during normal ship operations.

The composition of the waste stream resulting from different variations of components is given in the Table 1.

Slag Simulation Experiments

Several preliminary experiments were carried out to calculate the chemical composition of slag resulting from each variation in the waste stream: 1) Determination of the oxidation behavior of steel and, 2) Determination of the content of inorganic compounds in copier paper (about 69% of all waste paper).

The oxidation of steel (chopped #10 steel can) contained in an aluminosilicate boat was conducted by heating for 4 hours at 1400°C in air. This temperature was selected based on guidance from the designers and because 1400°C can be considered the maximum use temperature for the refractories being considered. As it shown in Figure 1 (X-ray), steel was oxidized to a mixture of magnetite (Fe_3O_4) and hematite (Fe_2O_3). The aluminosilicate boat used for the experiment had some signs of corrosion, indicating the unsuitability of aluminosilicate refractories for melting iron-containing materials.

¹ Eugene E. Nolting, et al, "Navy Shipboard Plasma Arc System Development Program," and Roy V. Richard, et al, "Navy Shipboard Plasma Arc Waste Destruction System (PAWDS) Baseline Conceptual Design," *Proceedings of the International Conference on Incineration and Thermal Treatment Technologies*, May 12-16, 1997.

The content of inorganic compounds was determined for three brands of copier paper. The papers exhibited about 16 wt. % ash after burning and a final residual of about 9 wt. % of inorganic compounds after calcining in the 800-1300°C range. The compounds found after calcining were CaO in two brands and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and SiO_2 in the other brand. Figures 2 and 3 show the X-ray diffraction patterns of these residues. Papers yielding CaO ash actually contain CaCO_3 (calcium carbonate) and papers yielding mullite & silica actually contain kaolin clay (kaolinite - $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ as a major compound) as a filler.

Paper companies have indicated that the filler content can vary from 6 to 25%, and the fillers can consist of calcium carbonate, clay, titanium dioxide, and others, and may be used in various combinations. The results of this experiment highlight the importance of the paper composition, since both the ash content and composition can affect a gas flow in the chamber, slag melting temperature, its viscosity, and corrosive attack on refractories. The presence of the ash in the PAWDS has serious design implications, as it can be carried out with the gas effluent and require separation, or can precipitate on the chamber walls causing wall (refractory) corrosion and caking/clogging problems, or may go into the slag pool inconsistently (depending on gas flow and feed rate) causing variable slag properties.

The composition of the slag was calculated for all suggested variations in feed composition based on the following assumptions:

1. Steel and aluminum cans will be oxidized to Fe_3O_4 and Al_2O_3 , respectively.
2. The paper contains 1) 16 wt.% calcium carbonate filler (yielding about 9 wt.% CaO on decomposition), or 2) 9.5% kaolin filler (yielding 9% mullite on decomposition), or 3) 15 wt.% of 50% CaCO_3 / 50% kaolin filler (yielding 10 wt.% of a mixture of CaO, mullite, and silica on decomposition). The latter assumption on the filler composition was selected based on the reality of having a mixture of paper containing both types of fillers in the shipboard waste stream. Accordingly, the slags in the simulation experiments were designated as Nominal 1, Nominal 2, and Nominal 3 depending on the filler composition in the paper, respectively.
3. All minerals from paper get into the slag pool after combustion.
4. Alloying elements in steel (e.g. Mn, P, S, C, Si, Cr, etc.) which cumulatively total 1-2 wt. % of steel have no effect.
5. No tin coating on steel cans.
6. Food waste contains 10 wt. % of bone, and bone is 75 wt. % $\text{Ca}_{10}\text{P}_6\text{O}_{26}\text{H}_2$.
7. Melting will be conducted in oxidizing atmosphere (air).

Calculated chemical compositions of slags containing all three types of paper fillers are given in Table 2.

All the initial slag simulation research was conducted with the Nominal 1 slag based on paper containing CaCO_3 as a filler. The slags were prepared for each variation in the waste stream using the following experimental conditions:

1. Starting materials: chopped Navy #10 steel cans, aluminum soda cans, crushed glass bottles, CaCO_3 , and phosphoric acid. Paper ash was assumed to be all CaO, and bone was simulated using CaCO_3 and H_3PO_4 to yield $\text{Ca}_{10}\text{P}_6\text{O}_{26}\text{H}_2$.

2. Batch size: 30 - 40 g.
3. Crucible for melting slags: fully dense aluminum oxide (corundum).
4. Atmosphere: air.
5. Heating conditions: 1400-1500°C with different heating rates (from 2°C to 10°C/min) and holding times (15 minutes to 2 hours).

Table 3 shows the chemical composition of all possible excursions in the waste stream on the basis of Nominal 1 slag.

Table 4 and Figure 4 show the results of slag simulation experiments conducted by heat treatment of the wastes at 1400°C for 2 hours with 3°C/min heating rate. Photographs on Figure 4 show the resulting slags in sectioned aluminum oxide crucibles. The data indicate that Nominal 1, Zero Aluminum, and Zero Glass excursions formed molten slags. Compared to that, the slags resulting from the Zero Paper and Zero Steel excursions were not fully molten. These slags as well as the Nominal 2 and Nominal 3 slags were fully molten only at 1500°C (Figure 5).

No noticeable corrosion of the corundum crucibles was observed for the Zero Paper and Zero Steel excursions. The crucible containing solidified Zero Aluminum slag was corroded at the slag-crucible-atmosphere interface. This can be related to the intensive dissolution of Al_2O_3 from the crucible in $Na_2O - SiO_2 - Fe_2O_3$ (FeO) melt which formed on the surface of the slag during steel oxidation. On the basis of the phase diagram (Figure 6) the compositions in this system containing 30-60% SiO_2 and 20-40% Fe_2O_3 (in wt. %) will melt at 800 - 900°C. The formation of low-temperature and low-viscosity melt in the system is probably responsible for the complete melting and uniformity of the Zero Aluminum slag. The Zero Glass slag exhibited severe splashing of low viscosity melt and extensive corrosion and cracking of the alumina crucible (Figure 4).

An additional experiment was conducted on the Nominal 1 slag to determine the dependence of viscosity on temperature. A new specimen of slag was prepared as before, but was heated to 1500°C at heating rate of 4.5°C/minute and 2 hours holding time. The molten slag exhibited very low viscosity, and contained a small amount of iron droplets. The heating to 1500°C also did not result in any significant corrosion of the alumina crucible. This dramatic decrease in slag viscosity with a 100°C increase in temperature is of high practical importance in the design of the slag handling system.

The parallel high temperature slag melt was quenched by pouring into cold water (Figure 7). The quenched slag formed glassy "popcorn". The specific density of the quenched melt was determined using pycnometry and was 3.29 g/cm³. It is assumed that this value is close to the density of the molten slag and can be used for design considerations.

The differences in melting behavior between the various slags were analyzed in terms of oxide ratios in the slag compositions. The results are summarized in Table 5.

It can be concluded that only the Fe_3O_4/CaO ratio is well correlated with observed melting behavior of slags of various compositions. All slags (Nominal 1, Zero Aluminum, and Zero Glass), which melted during experiments, had close values of Fe_3O_4/CaO ratio in the range of 3.37 to 3.85. Significant deviations from this value in the slags Zero Paper and Zero Steel resulted only in partial melting. The results indicate the critical importance of the simultaneous

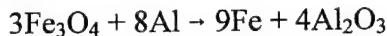
presence of calcium oxide and iron oxide as well as their ratio for decreasing the melting point and viscosity of slags.

To determine the range of $\text{Fe}_3\text{O}_4/\text{CaO}$ ratios leading to the melting slags at 1400°C , the melting behavior of slags with the $\text{Fe}_3\text{O}_4/\text{CaO}$ ratios of 1, 9, and 15 was characterized. The chemical composition of the slags is shown in Table 6 and their melting patterns are shown in Table 7 and Figure 8.

Simulation experiments conducted for the Nominal 2 (kaolin-containing paper) and Nominal 3 (kaolin/ CaCO_3 -containing paper) slags showed very limited melting at 1400°C (Figure 5) which can be related to high $\text{Fe}_3\text{O}_4/\text{CaO}$ ratio equal to 20.3 and 7.9, respectively. These two slags were fully molten only at 1500°C . In the absence of the CaCO_3 - containing paper, CaO should be added separately as CaCO_3 or some low-melting fluxes should be introduced to enhance the melting slags at temperatures close to 1400°C .

Development of the Thermite Reaction

The slags resulting from the Zero Glass excursions of Nominal 1,2 and 3 exhibited boiling and splashing, as well as severe cracking and melting of the crucible. This phenomenon is attributed to the very energetic thermite reaction taking place as a result of chemical interaction between iron oxides (FeO , Fe_2O_3 , and Fe_3O_4) and metallic aluminum. For example, the thermite reaction between Fe_3O_4 and Al by the reaction:



releases 838 kJ/mol of Al_2O_3 formed. The theoretical temperature created by this reaction is about 3200°C . Additions of non-reacting constituents, as well as heat loss to the reaction vessel and radiation reduce this temperature to about 2200 to 2400°C . The temperature for the initiation of the reaction was determined to be 1200°C by instrumenting the furnace with thermocouples and power input monitoring devices.

The heat generated by the reaction resulted in an instantaneous increase of temperature, probably in excess of 2050°C (the melting temperature of alumina) leading to cracking (due thermal shock) and melting of the crucible and leaking of the slags. In a full-scale shipboard reactor in Fleet conditions, the occurrence of the thermite reaction could result in the catastrophic damage to the whole system. Poor mixing of wastes components will, obviously, promote the localized thermite reaction which can also be damaging.

Thermogravimetry/differential thermal analysis (TG/DTA) was used to determine the oxidation and melting behavior of aluminum and steel, alone and in combination with components of the waste stream, especially with glass and CaCO_3 . The samples were heated at $20^\circ\text{C}/\text{min}$ up to 1400°C in an argon/oxygen atmosphere which simulated the concentration of oxygen in air.

The results of TG/DTA of aluminum and steel, alone and combined with glass and CaCO_3 , shown in Figure 9, 10, 11, and 12, verify that the oxidation behavior of steel and aluminum leads to conditions favorable for the development of the thermite reaction. In the DTA curves, the position of the peaks relative to the temperature axis indicates the temperature at which the maximum rate of a chemical reaction or phase transformation is occurring. For example, in the DTA curve of the aluminum in Figure 9, the endothermic peak at 665°C corresponds to the

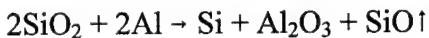
melting of aluminum, and the exothermic peak at 1375°C corresponds to the maximum rate of aluminum oxidation reaction ($4Al + 3O_2 \rightarrow 2Al_2O_3$). Also from Figure 9 and 10, the maximum oxidation rate for aluminum, whether it is alone or in combination with $CaCO_3$, occurs at 1375°C. However, the presence of $CaCO_3$ suppressed significantly the degree of aluminum oxidation which can be concluded from the height of $Al/CaCO_3$ DTA peaks. The oxidation temperature of Al is lowered to about 1200°C for the aluminum/glass combination (Figure 10). Thus, the presence of glass promotes the oxidation of aluminum.

In contrast, the maximum rate of steel oxidation ($3Fe + 2O_2 \rightarrow Fe_3O_4$) was observed at 1142°C (Figure 9). For the combination of steel with $CaCO_3$ (Figure 11), the maximum rate of oxidation took place at about 985°C; and for the steel/glass combination (Figure 11), three separate oxidation events occurred, with the first at 1118°C. Therefore, the maximum rate of oxidation of steel occurs at a temperature lower than that of aluminum. The high temperatures for oxidation of aluminum are due to the formation of a protective surface layer of aluminum oxide. The significance of the TG/DTA results is that it shows that during the processing of Navy wastes, steel will be oxidized before aluminum, creating favorable conditions for the occurrence of the thermite reaction.

For the thermite reaction in which Fe_3O_4 reacts with aluminum according to $3Fe_3O_4 + 8Al \rightarrow 9Fe + 4Al_2O_3$, the Fe_3O_4 / Al ratio (by weight) for this stoichiometric reaction is 3.22. In the Nominal 1 Navy waste stream (Table 1), if iron is assumed to be completely converted to Fe_3O_4 (neglecting carbon and other alloying elements in the steel), the Fe_3O_4 / Al ratio would be 3.27. Hence, even the *nominal* Navy waste stream has the potential to create a near stoichiometric thermite reaction during processing. The metallic droplets occasionally observed in the Nominal 1 slags probably have to be considered as "secondary" iron formed and melted in the course of the thermite reaction. (see reaction in the beginning of the paragraph). The thermite reaction was more noticeable during fast heating of the slag (Figure 13) confirmed by the presence of much high amount of "secondary" iron. This behavior can become a serious problem in fast-heating conditions of a real reactor.

The occurrence of the thermite reaction only in the Zero Glass excursion suggests the critical importance of the presence of a glass melt (glass melting temperature was determined to be about 1050°C) for suppression of the reaction.

The protective function of the glass melt is probably the result of physical separation of aluminum from iron oxide, as well as, the result of an oxidation-reduction reaction in which silica in the glass is reduced by aluminum according to the reaction:



to form silicon, alumina, and silicon monoxide (gas). By this reaction, metallic aluminum is oxidized about 800°C and is not available for participation in the thermite reaction (ignition temperature about 1200°C) with iron oxides. Experimental confirmation of the occurrence of the oxidation-reduction reaction was provided by heating (in air and in helium) pieces of aluminum buried in crushed bottle glass to 1400°C for 30 minutes. Regardless of the atmosphere in the furnace, the same results were observed (Figure 14): a black coloration of the glass melt indicating the presence of elemental silicon which was confirmed by x-ray photoelectron spectroscopy (XPS), and bubbles in the melt, particularly at the aluminum/glass interface, suggesting the formation of gaseous SiO . Much more severe thermite reaction in the

fast-heating experiments (10°C/min heating rate compared to 2°C/min) can probably be a result of insufficient degree of Al oxidation with SiO₂ by the above reaction.

To identify the minimum content of glass required for the suppression of the thermite reaction, the series of waste compositions was investigated having 15, 30, and 50 wt. % of glass normally present in the *nominal* waste stream. Experiments were conducted using Nominal 1 waste stream (CaCO₃ - containing paper) as a baseline. The wastes composition and chemical composition of the slags are given in Table 8 and 9.

The 15, 18% and 30% glass excursions exhibited severe thermite reactions and destruction of the alumina crucibles shown in Figure 15. No significant thermite reaction was observed in the slag containing 50% of the *nominal* glass content. Thus, at least 50% of the glass as contained in the *nominal* waste stream is necessary to prevent the thermite reaction during the thermal destruction of Navy wastes.

As it was mentioned above, even the Nominal 1 Navy waste stream compositions have the potential to develop thermite reaction during processing. The metallic droplets occasionally observed in the Nominal 1 slags and that were considered as "secondary" iron from the thermite reaction confirm the occurrence of the reaction. To characterize the effect of excess of glass on melting behavior of the slags and development of thermite reaction the slags containing 25 and 50% excess of glass were prepared and evaluated. The composition of the waste stream and slags are shown in Tables 10 and 11 and their melting behavior are shown in Figure 16 and Table 12. The data indicate that slags with excess of glass have improved melting behavior compared to the Nominal 1 slag. The slags did not contain any "secondary" iron droplets proving that the thermite reaction did not occur during melting experiments.

Prevention of the Thermite Reaction

To prevent the thermite reaction in the case of the total absence of glass in Fleet conditions at sea, silicon oxide-containing alternative materials were investigated. Sand was selected as the primary substitute for glass, based on its availability and low cost. However, the introduction of sand as 100% replacement for glass in the Nominal 1 waste stream composition also resulted in a severe thermite reaction (Figure 17). The occurrence of the thermite reaction during the processing of the sand-containing waste stream can be related to the very high melting temperature of sand (about 1700°C) resulting in the absence of a melt at temperatures below the ignition point of the termite reaction (1200°C).

Based upon this result several **low-melting fluxes** were investigated to substitute glass in the Nominal 1 waste stream:

- Combinations of sand and sodium bicarbonate (NaHCO₃) or soda with SiO₂ : Na₂O ratios of 3:1, 2:1, and 1:1 by weight
- Sodium silicate (water glass) of composition Na₂O • 3.22 SiO₂ (SiO₂ : Na₂O = 3.22 : 1)
- Sodium/potassium/calcium feldspar (0.8(Na_{0.72} K_{0.28})AlSi₃O₈ / 0.2(CaAl₂Si₂O₈))
- Pure Sodium bicarbonate (NaHCO₃)

On the basis of the SiO_2 - Na_2O phase diagram (Figure 18), the melting temperatures of the selected sand/soda combinations with SiO_2 : Na_2O ratios of 3:1, 2:1, and 1:1 are about 793, 874 and 1089°C, respectively. To determine the minimum amounts of the mixtures required to prevent the thermite reaction, all three fluxing mixtures with SiO_2 : Na_2O ratios of 3:1, 2:1, and 1:1 were introduced at 15 to 100% of the normal glass content. The chemical composition of the slags is given in Tables 13, 14, and 15.

As shown on Figures 19, 20, and 21, the addition of only 30% sand/soda mixtures with the SiO_2 : Na_2O ratios of 3:1 and 2:1 as a replacement for glass resulted in the complete suppression of the thermite reaction, while a 60% substitution of the mixture for the *nominal* glass content was required when the SiO_2 : Na_2O ratio was 1:1. The latter can be attributed to much higher melting temperature of the 1:1 mixture, compared to 3:1 and 2:1 ones, which was probably interfering with the maximum realization of melt protective capabilities. Table 16 summarizes the chemical and physical transformations in slags during heating and their effects on the development of the thermite reaction. The Nominal 1 slag with SiO_2 : Na_2O (NaHCO_3) ratio of 2:1 was selected as an example.

The melt, uniformly distributed between the waste particles, creates conditions for both physical and chemical means to prevent the thermite reaction, as observed in the bottle glass-containing slag with glass melting temperature about 1050°C. Contrary to that, in the sand-containing slag (melting point of sand is about 1700°C), no silica-containing melt exists below 1200°C to prevent the thermite reaction. In the slag containing sand and soda with SiO_2 : Na_2O ratios of 2:1, melt existed at temperatures above 874°C creating conditions for much longer exposure of metallic Al to the low viscosity silicate melt. In this case only 30% substitution for glass was required for the suppression of the thermite reaction.

The thermite - reaction suppressing effectiveness of fluxes introduced in the form of sodium silicate compounds, instead of the mixed oxides (sand plus soda), was investigated. The introduction of compounds was expected to be more efficient than that of mixed oxides. Sodium silicate (soluble or water glass) of composition $\text{Na}_2\text{O} \cdot 3.22 \text{SiO}_2$ (SiO_2 : Na_2O = 3.22 : 1) with a melting temperature about 800°C was selected as a primary candidate. The water glass had a composition similar to the sand - soda mixture (SiO_2 : Na_2O = 3:1) used previously. The additives were introduced at 15 to 100% of the *nominal* glass content. Similar to the sand - soda mixture, the thermite reaction was suppressed by the introduction of 30% of water glass (Figure 22). Table 17 shows the chemical composition and melting behavior of the resulting slags. An embedded iron nodule in the crucible containing slag with 15% substitution of glass with sodium silicate is a "secondary" iron which was formed as a result of the thermite reaction. From the practical equality of the weight of steel in the starting mixture and the iron nodule, it can be concluded that all present steel was oxidized and participated in the thermite reaction forming molten "secondary" iron.

In the next approach sodium/potassium/calcium feldspar ($0.8(\text{Na}_{0.72}\text{K}_{0.28})\text{AlSi}_3\text{O}_8 / 0.2(\text{CaAl}_2\text{Si}_2\text{O}_8)$) with melting temperature of about 1100°C as 15-100% substitution for glass in the Nominal 1 slag composition. In this case Na_2O , K_2O , and SiO_2 were also bonded in the chemical compound. Table 18 and Figure 23 show the chemical composition and melting behavior of the slags.

Compared to sand-soda mixture and water glass, the thermite reaction was suppressed only after substitution of 65% of feldspar for glass. The significant difference in the amounts of the

sodium silicate fluxes required to suppress the thermite reaction is probably due to the differences in their melting temperature and viscosity which are both higher for the feldspar. The nature of the sodium oxide / silica - based fluxes (chemical compound or oxide mixtures) did not affect their effectiveness in suppressing the thermite reaction.

Sodium bicarbonate (NaHCO_3) alone (without combination with SiO_2) was also used to suppress the thermite reaction in the total absence of glass in the waste stream. The chemical composition and development of the thermite reaction of slags with various Na_2O content are given in Table 19. The data show that the thermite reaction was suppressed in the slag containing 60% Na_2O as a substitution for glass. In this composition, total Na_2O content is equal to 9.98% compared to 2.14% in the Nominal 1 slag which contains 11.31% of SiO_2 . The results confirms again the importance of simultaneous presence of sodium oxide and silica for effective suppression of the thermite reaction.

There are no compositions in the Na_2O - CaO - Al_2O_3 - Fe_2O_3 quaternary system with melting temperatures below 1175°C. In this case, a significant amount of Na_2O -rich liquid was necessary for the prevention of the thermite reaction using only particle-separation mechanism at temperatures below 1200°• (ignition temperature).

Thus, the most important requirement for suppression of the thermite reaction is the presence of a silicon oxide-containing melt prior to the ignition point of the thermite reaction (1200°C). The melting temperature of flux strongly influences its effectiveness. Low melting additives, such as sodium silicates with the melting temperatures below 900°C, allow the melt to have a longer exposure time with the solid components of the slag for the effective use of both the physical and chemical protective mechanisms which results in a significant decrease in the amount of the flux required to suppress the thermite reaction. In addition, the viscosity of a low melting flux is expected to be significantly lower at temperatures near 1200°C compared to that of a high melting flux. The low viscosity additionally contributes to the flux effectiveness as a result of better distribution of the melt among solid particles allowing much thinner intergranular layers and thus further decrease in a necessary flux content. The advantage of using low melting/low viscosity fluxes is illustrated in Table 20 and Figure 24.

The results show that the melting temperature of the flux correlates directly with the amount of the additive required to suppress the thermite reaction. The additives which melt at lower temperatures are required in smaller amounts than those which melt at higher temperatures. The total silica content in the slag, which depends on both flux amount and composition, does not correlate as well with the melting temperature because of the confounding effect of flux melt viscosity. For example, the two highest melting fluxes, sand/soda with $\text{SiO}_2:\text{Na}_2\text{O}=1:1$ (m.p. 1089°C) and feldspar (m.p. 1100°C), which are required in approximately the same amounts (60 and 65%, respectively), have widely different SiO_2 contents (5 and 7.3%, respectively) in the slag. The higher silica content required to prevent the thermite reaction in the feldspar-containing slag can probably be attributed to a much higher viscosity of feldspar melt compared to that of sand/soda melt.

The effect of a SiO_2 / Al ratio in the slags on the development of the thermite reaction is very well correlated with the SiO_2 content and shown in Table 21.

The experiments conducted with Nominal 2 and 3 slags showed that all the fluxes, which suppressed the thermite reaction in Nominal 1 (CaCO_3 - containing paper), acted similarly when introduced into Nominal 2 (kaolin -containing paper) and Nominal 3 (50% kaolin / 50% CaCO_3 -

containing paper). However, for these slags, the fluxes which prevented the termite reaction did not promote their melting. The slags required heating to 1500°C for complete melting compared to 1400°C for Nominal 1 slags which contained the same fluxes. The introduction of borax - $Na_2B_4O_7$ with melting temperature of 742°C led to the complete melting of the Nominal 2 & 3 slags at 1400°C as a result of the formation of low-melting aluminoborosilicate glass. However, the use of borax as a flux is questionable because of its active evaporation above 1100°C.

Conclusions

The laboratory slag modeling experiments were conducted to determine the melting behavior of slags during plasma-arc destruction of Navy wastes in an oxidizing atmosphere. The melting behavior of slags is a strong function of waste stream composition and processing parameters. A severe thermite reaction was observed in the Zero Glass excursion of the waste stream at about 1200°C as a result of the chemical interaction between iron oxides and aluminum. The occurrence of the thermite reaction only in the Zero Glass excursion suggests the critical importance of the presence of a glass melt (glass melting temperature was determined to be about 1050°C) for suppression of the reaction.

The protective effect of a glass melt is a result of physical separation of aluminum from iron oxides, as well as, the low temperature (about 800°C) oxidation of Al by the reduction of SiO_2 . The oxidation of aluminum below 1200°C makes the thermite reaction impossible. At least 50% of the glass as contained in the *nominal* waste stream is required to prevent the thermite reaction. The introduction of sand as replacement for glass did not prevent the thermite reaction, confirming the importance of melt.

In the absence of glass, the thermite reaction was suppressed by the introduction of the sand/soda mixture and sodium silicates with various SiO_2 / Na_2O ratios or by sodium/potassium feldspar. The amount of flux required to suppress the thermite reaction depends on flux chemical composition, melting temperature, and viscosity. The additives which melt at lower temperatures and have lower viscosity are required in smaller amounts than those with high melting temperature and viscosity. For example, the minimum content of fluxes introduced as substitution for the *nominal* glass content was 60% for feldspar (melting temperature about 1100°C, high viscosity) and 30% for the sand/soda mixture with SiO_2 / Na_2O ratio equal to 3:1 (melting temperature about 800°C and low viscosity).

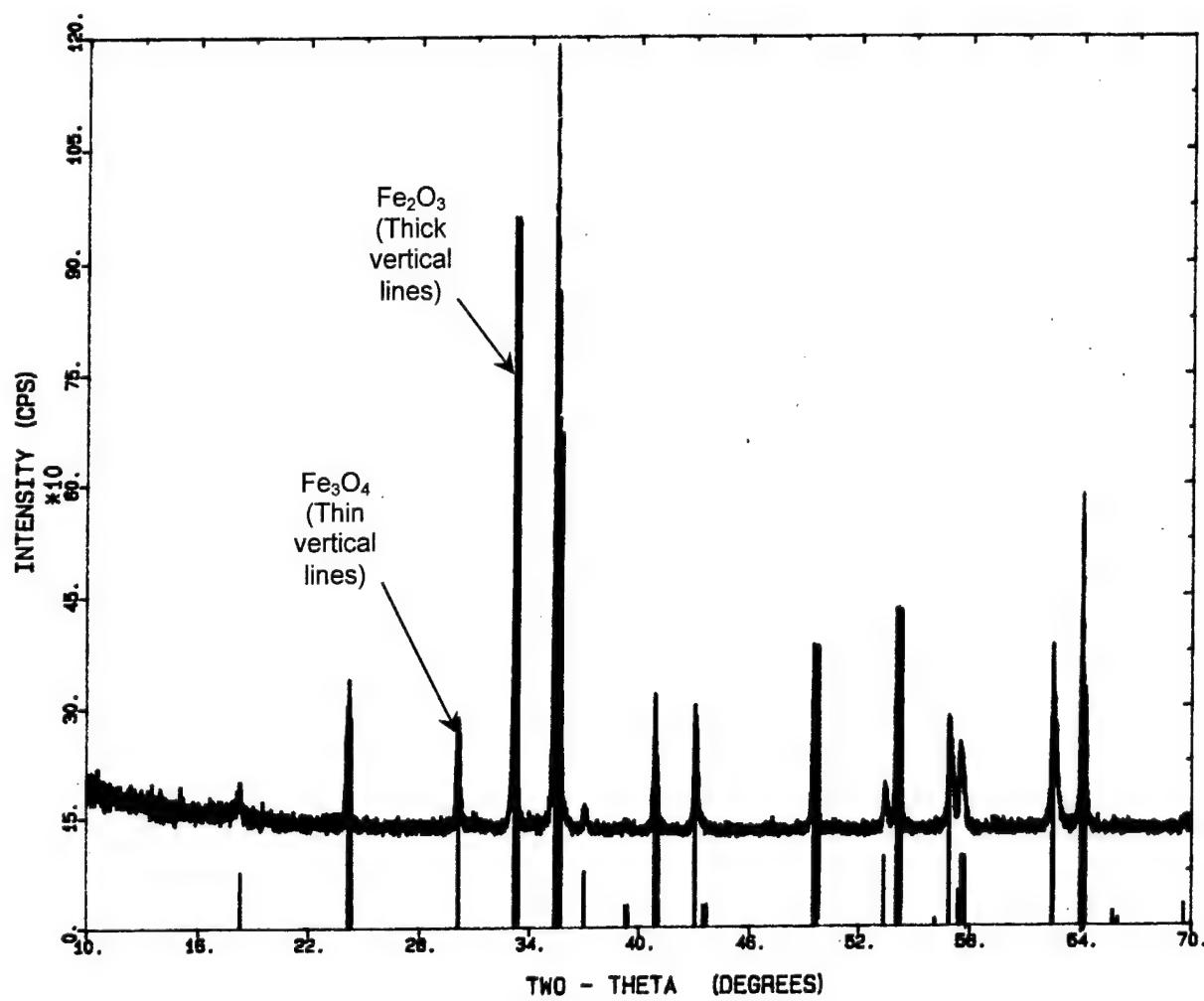


Figure 1. XRD of Steel Oxidized at 1400°C.

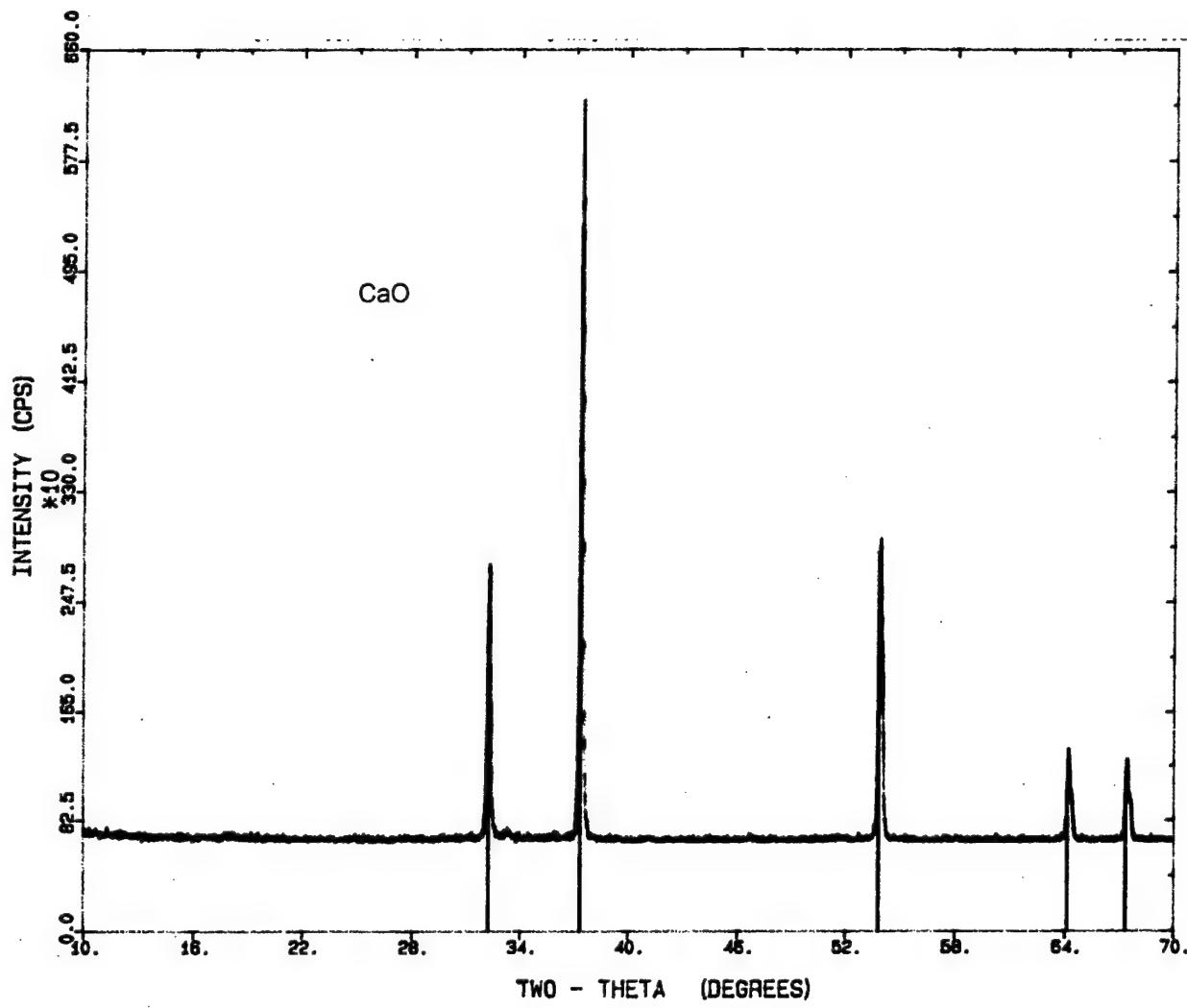


Figure 2. XRD of Copy Paper #1 (CaCO₃ - containing paper).

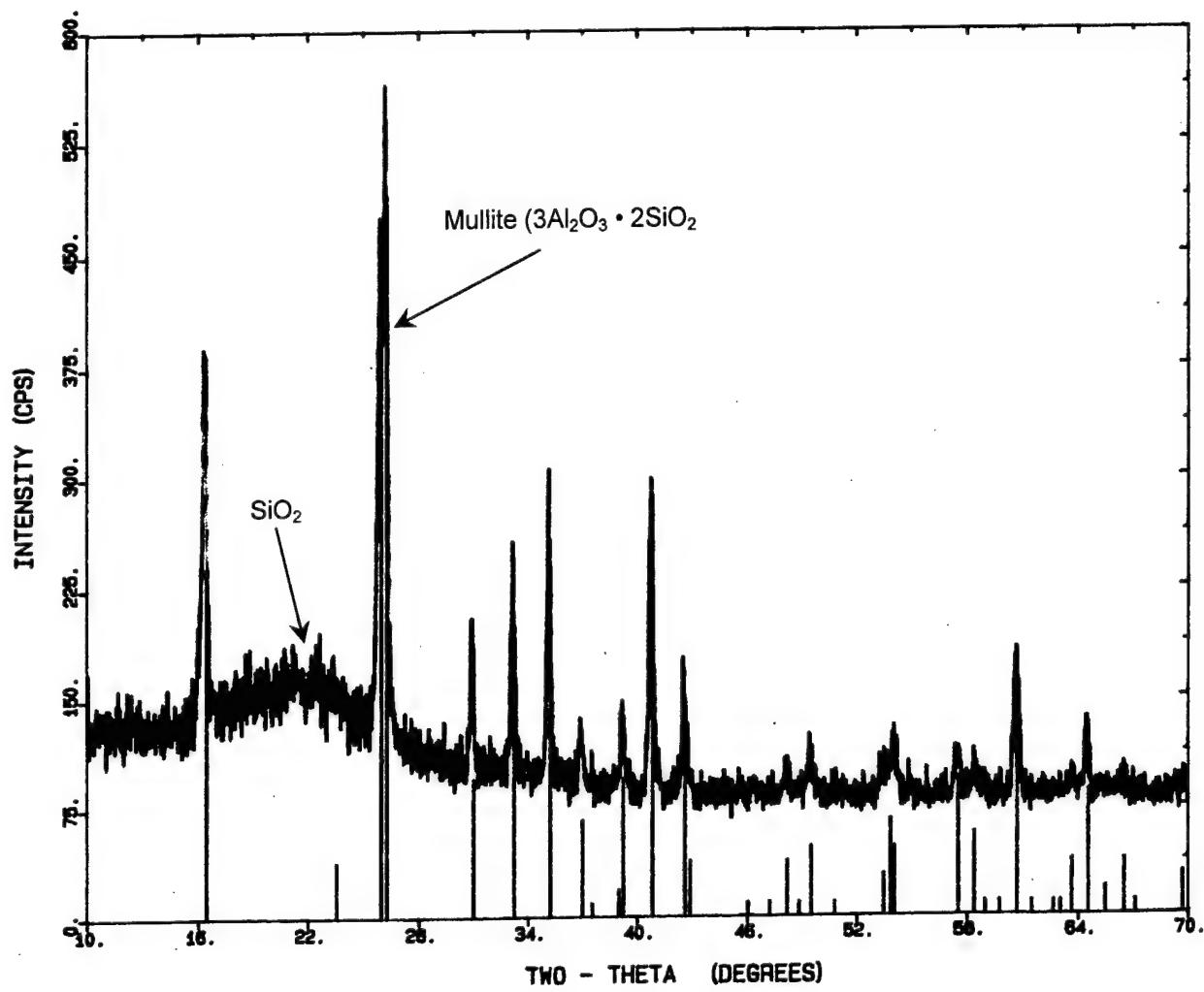


Figure 3. XRD of Copy Paper #2 (Kaolin - containing paper).

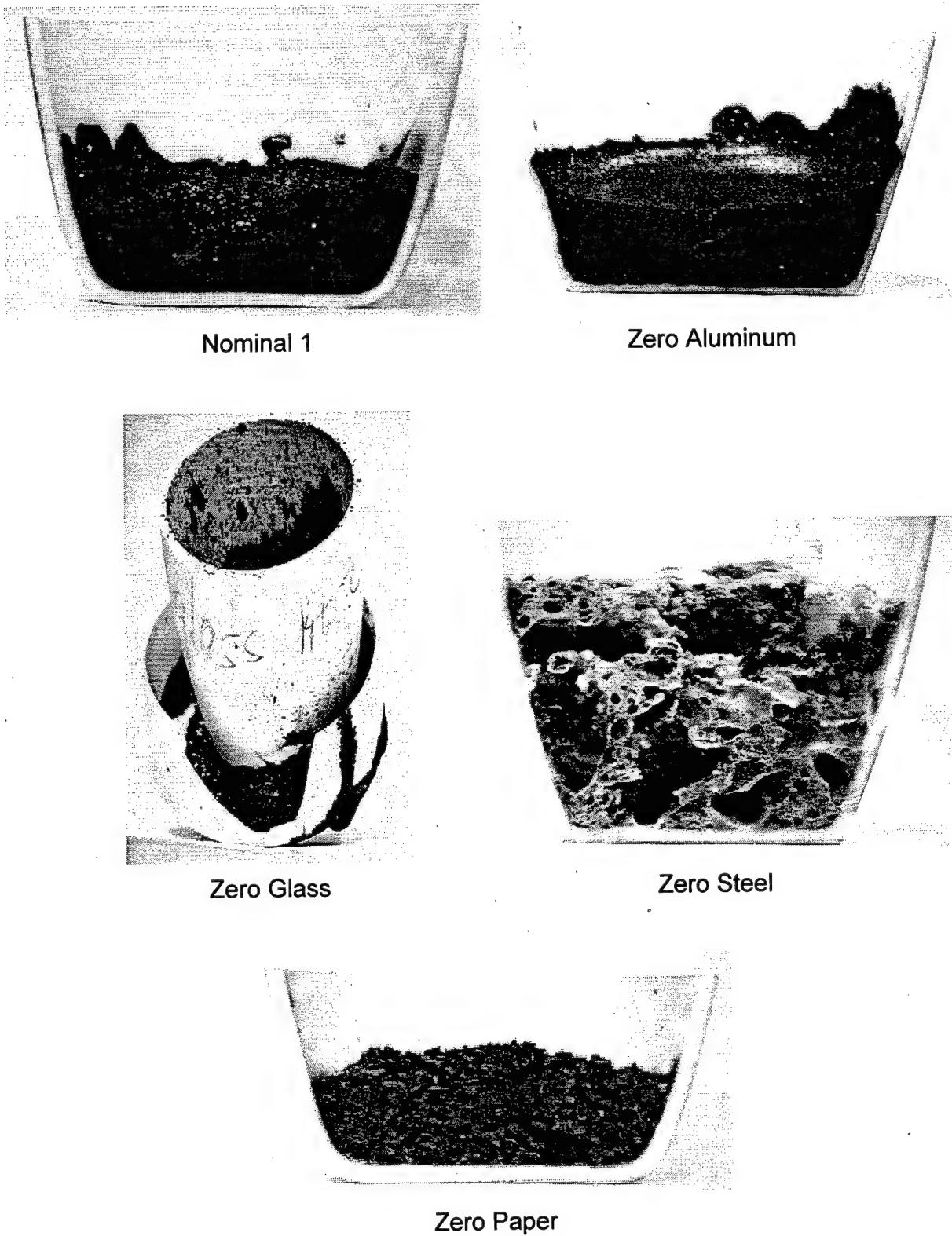
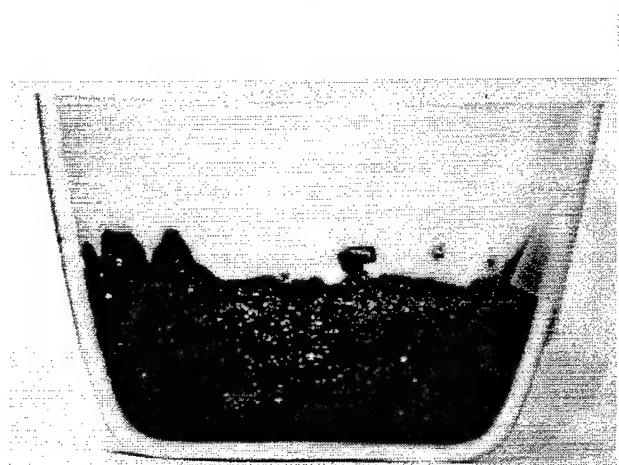
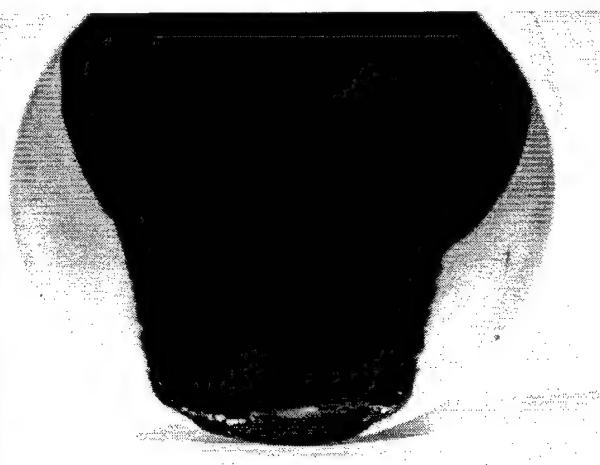


Figure 4. Heating Behavior of Slag Composition Excursions (Heating Conditions: 1400°C for 2 hours, heating rate 3°C/minute).

1400°C



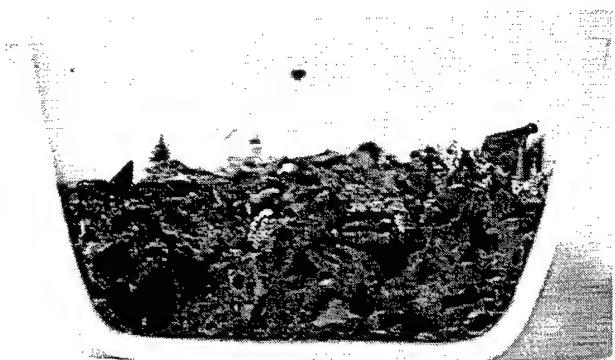
1500°C



Nominal 1, CaCO_3 Filler



Nominal 2, Kaolin Filler



Nominal 3, 50/50 CaCO_3 /Kaolin Filler

Figure 5. Melting Behavior of "Nominal 1,2,3" Slags at 1400°C and 1500°C.

Na₂O-Fe₂O₃-SiO₂ (cont.)

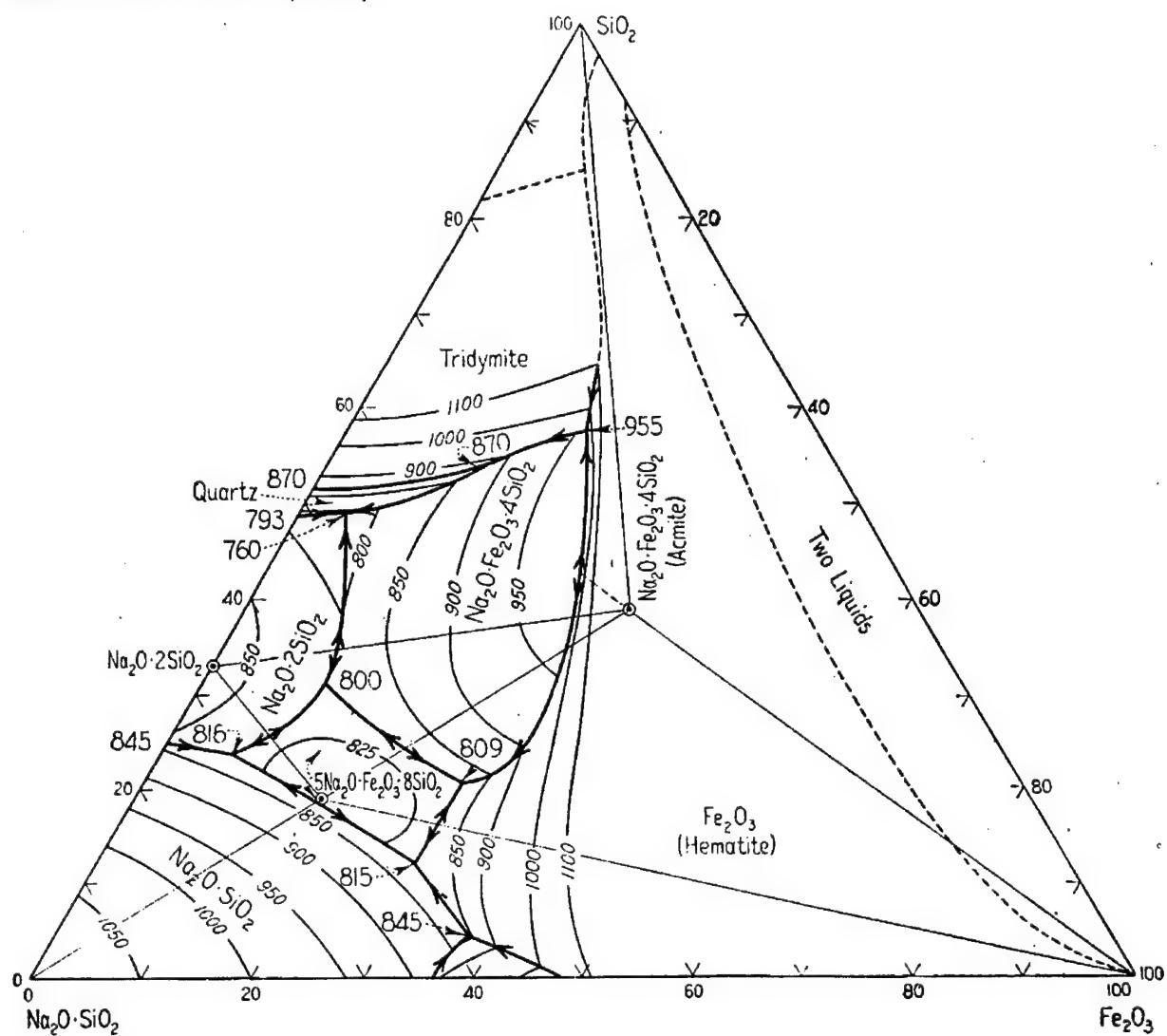


Figure 6. System $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O} \bullet \text{SiO}_2$.²

² Levin, E.M., C.R. Robbins and H.F. McMurdie, editors. *Phase Diagrams for Ceramists*, Figure 520, The American Ceramic Society, Inc. 1964. N.L. Bowen, J.F. Schairer and H.W. Williams, *Am. J. Sci., 5th Ser.*, **20**, 419, 1930.

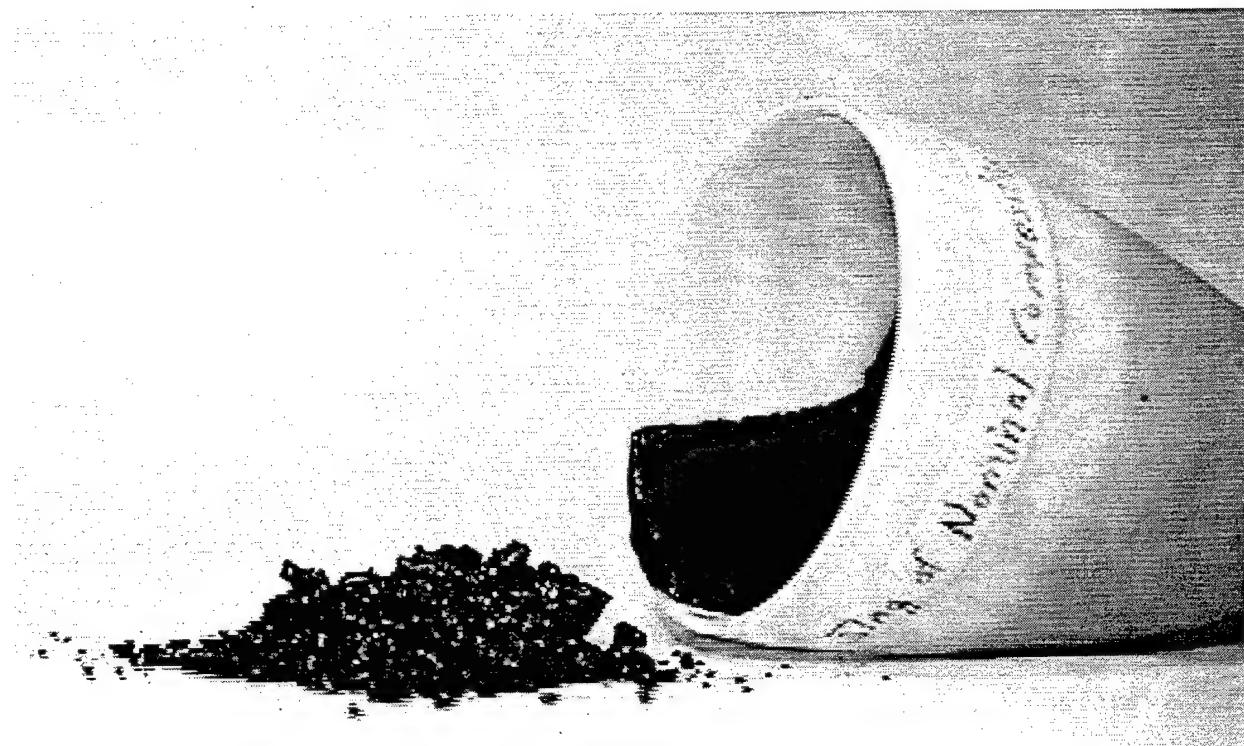


Figure 7. Melting Behavior of "Nominal 1" Slag at 1500°C (Granules formed during quench in water).

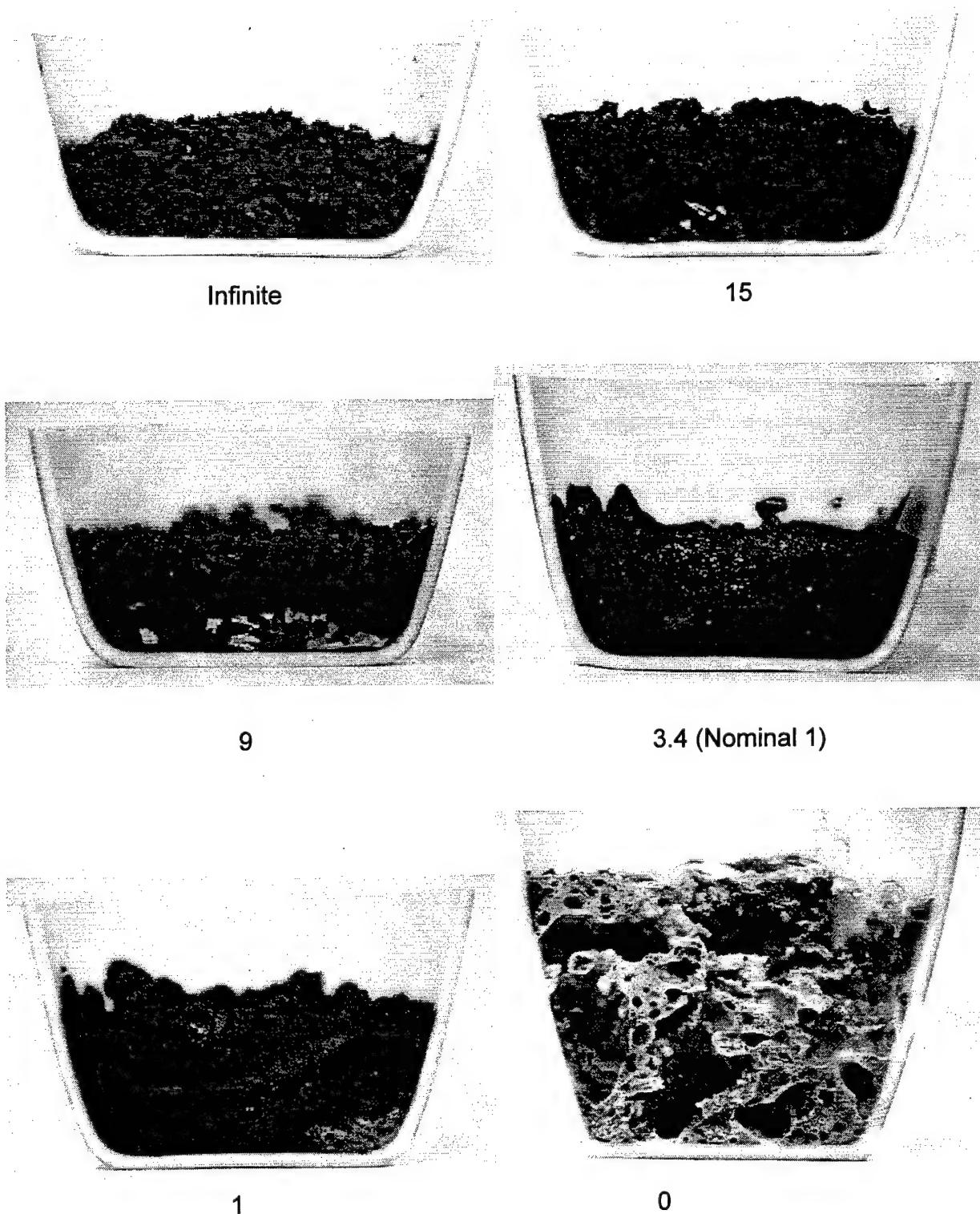


Figure 8. Effect of $\text{Fe}_3\text{O}_4/\text{CaO}$ Ratio on Slag Melting Behavior (Heating Conditions: 2-hour hold at 1400°C)..

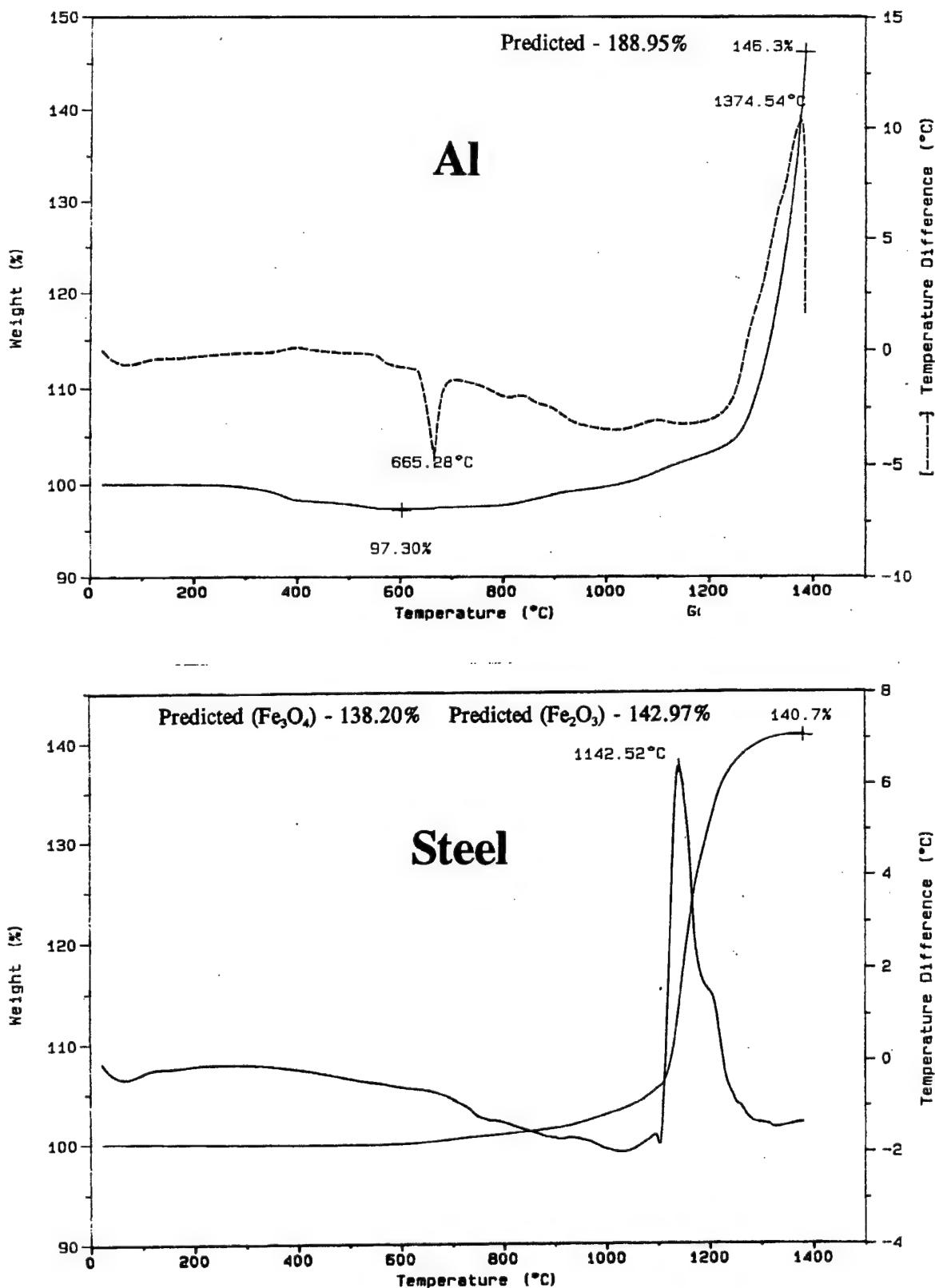
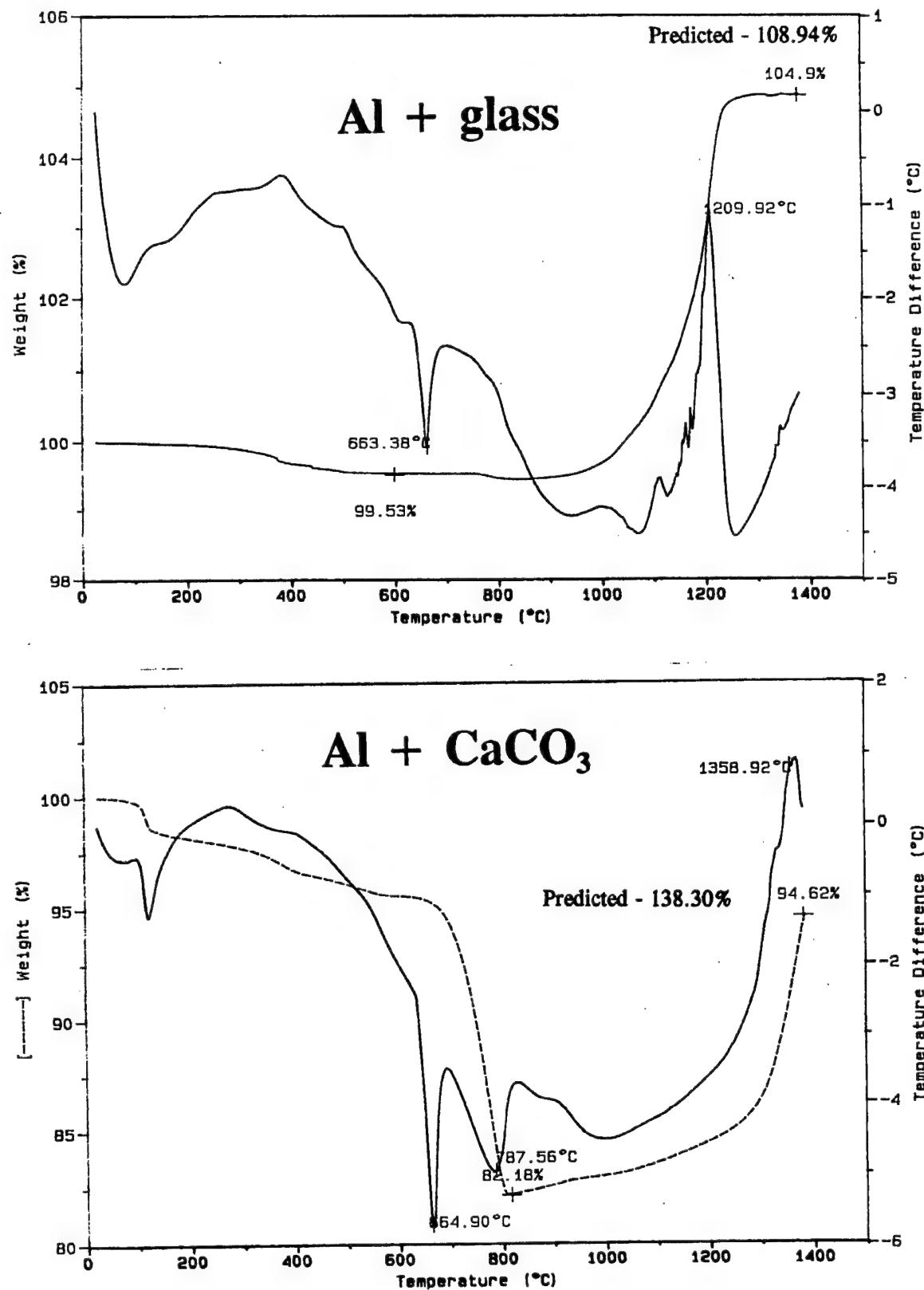
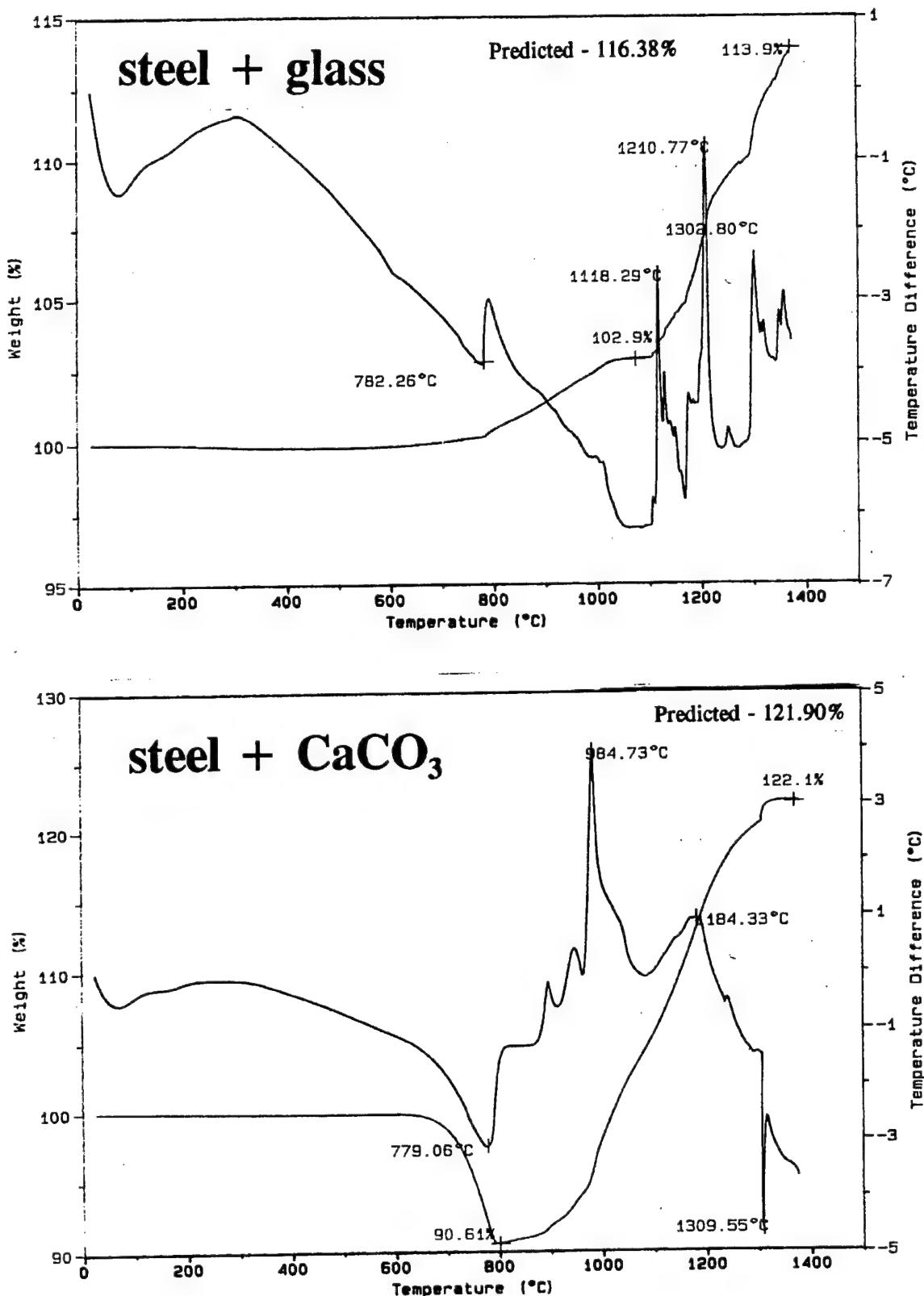
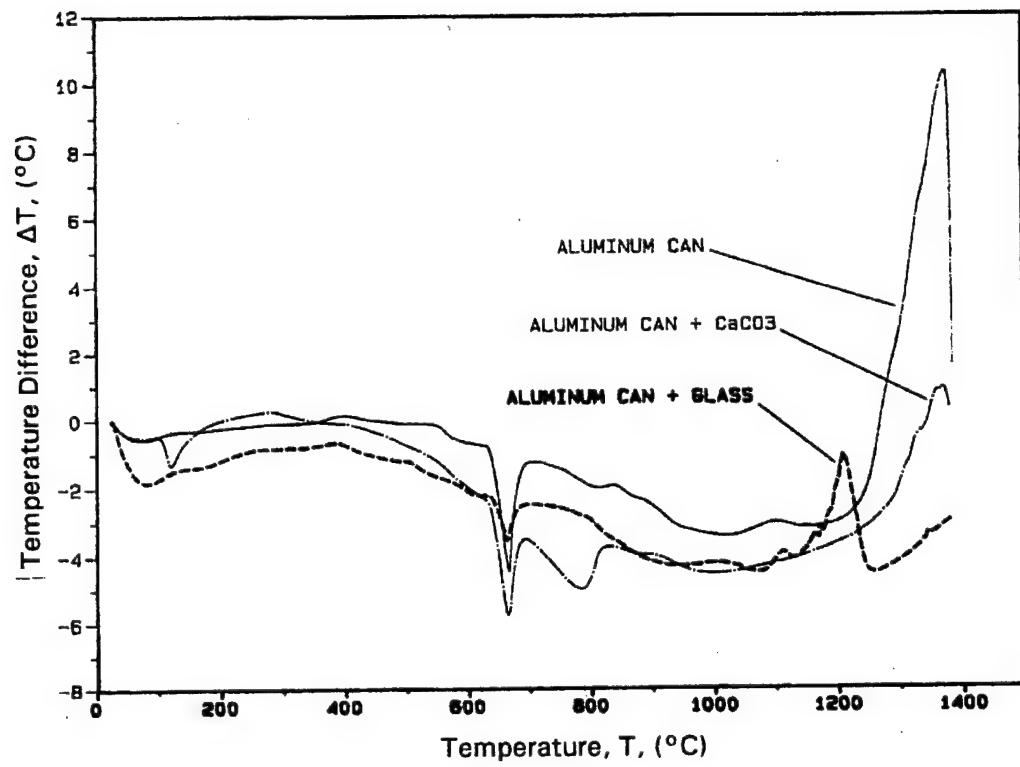


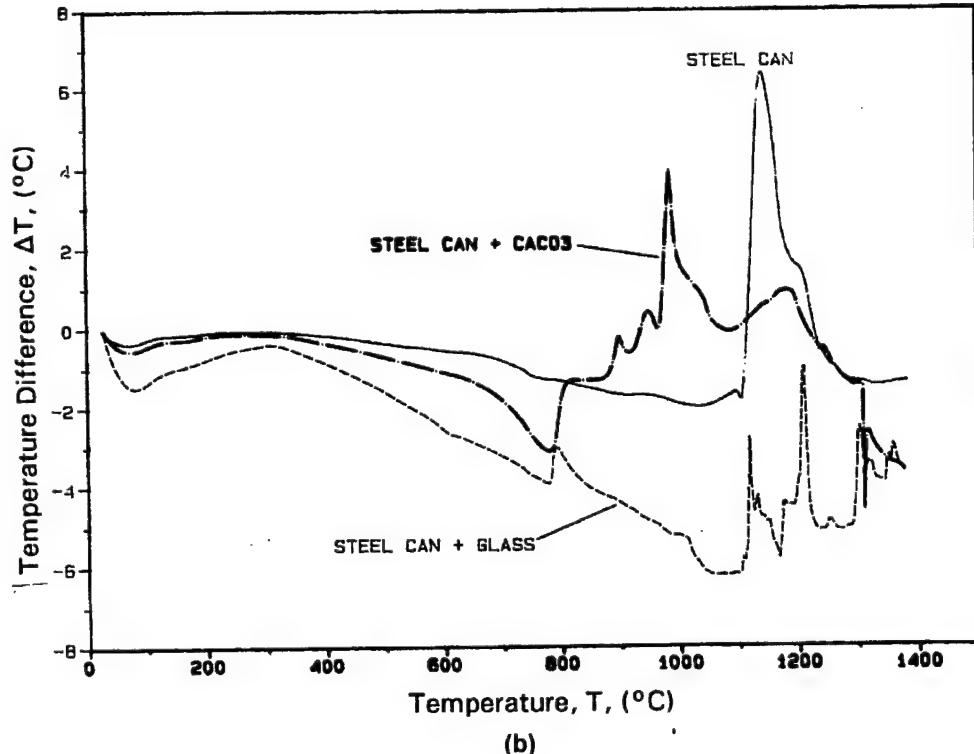
Figure 9. TG/DTA for Aluminum and Steel Cans.

Figure 10. TG/DTA of Steel with Glass and CaCO₃.

Figure 11. TG/DTA of Steel with Glass and CaCO₃.



(a)



(b)

Figure 12. DTA of Aluminum and Steel.

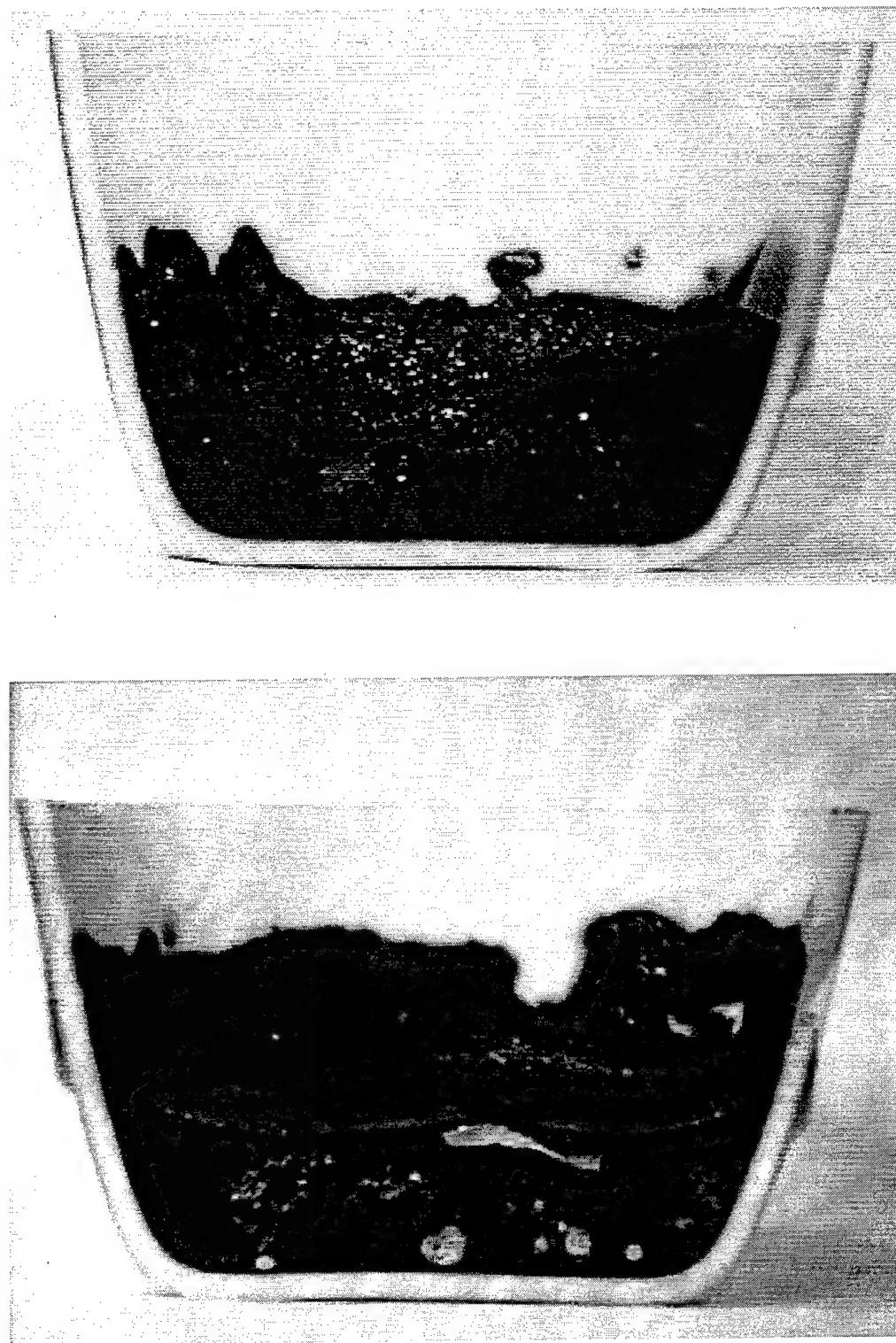


Figure 13. Effect of Heating Rate on the Development of Thermite Reaction in the "Nominal 1" Slag.

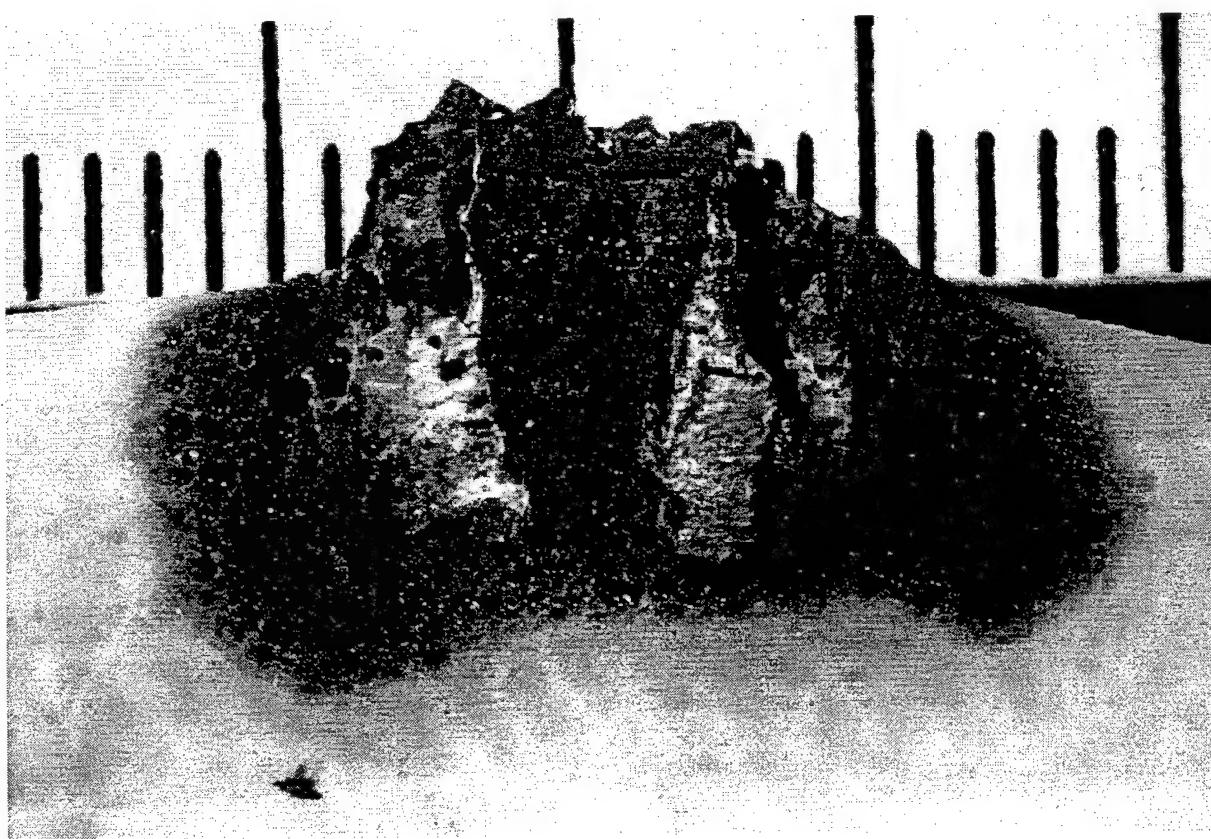


Figure 14. Cross Section of Coiled Aluminum Strip Heated in Bottle-Glass Melt.

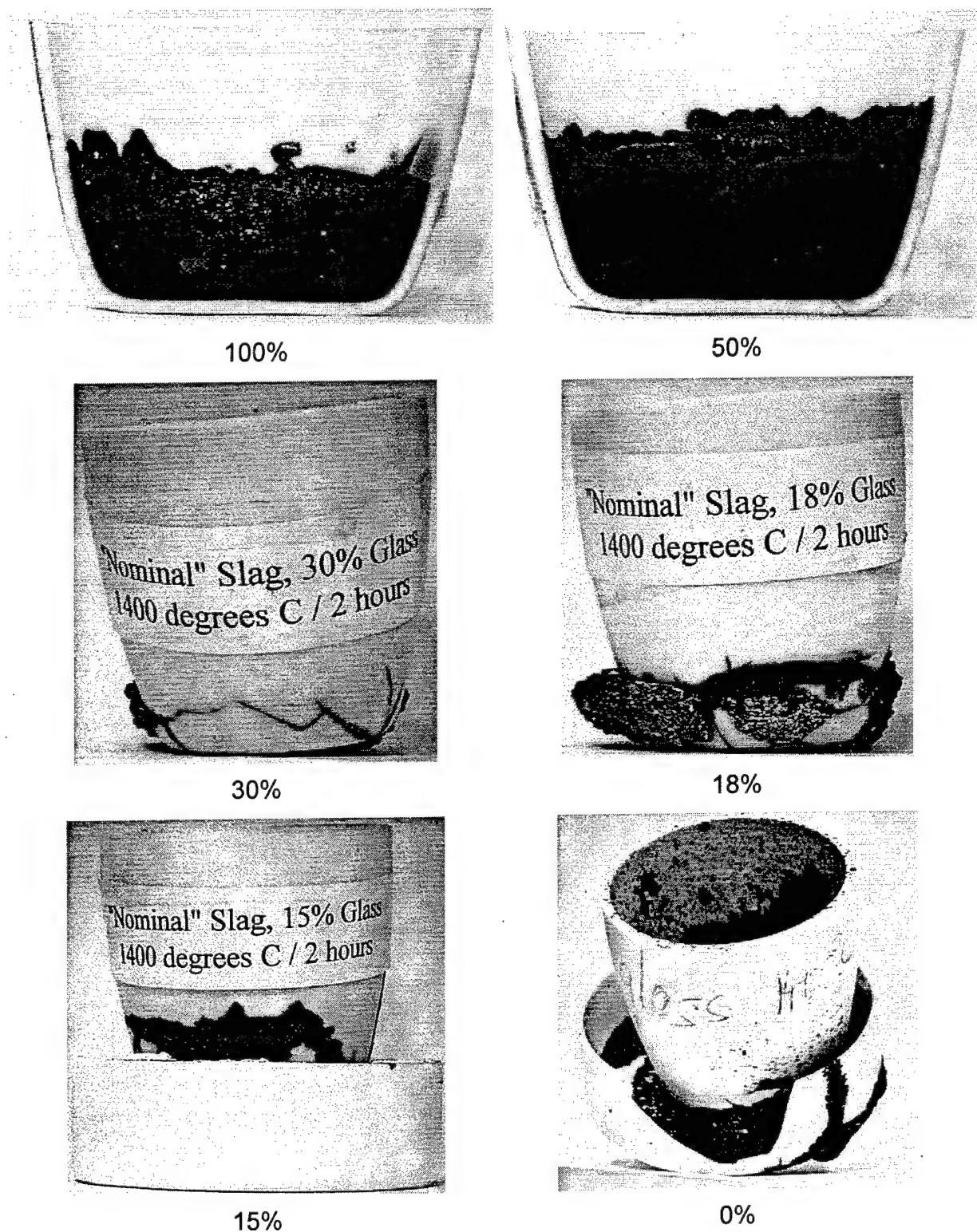


Figure 15. Variation of Glass Content in Nominal Slag Composition (Values are in percent of glass in nominal slag which is 7.34%. Heating Conditions: 2-hour hold at 1400°C).

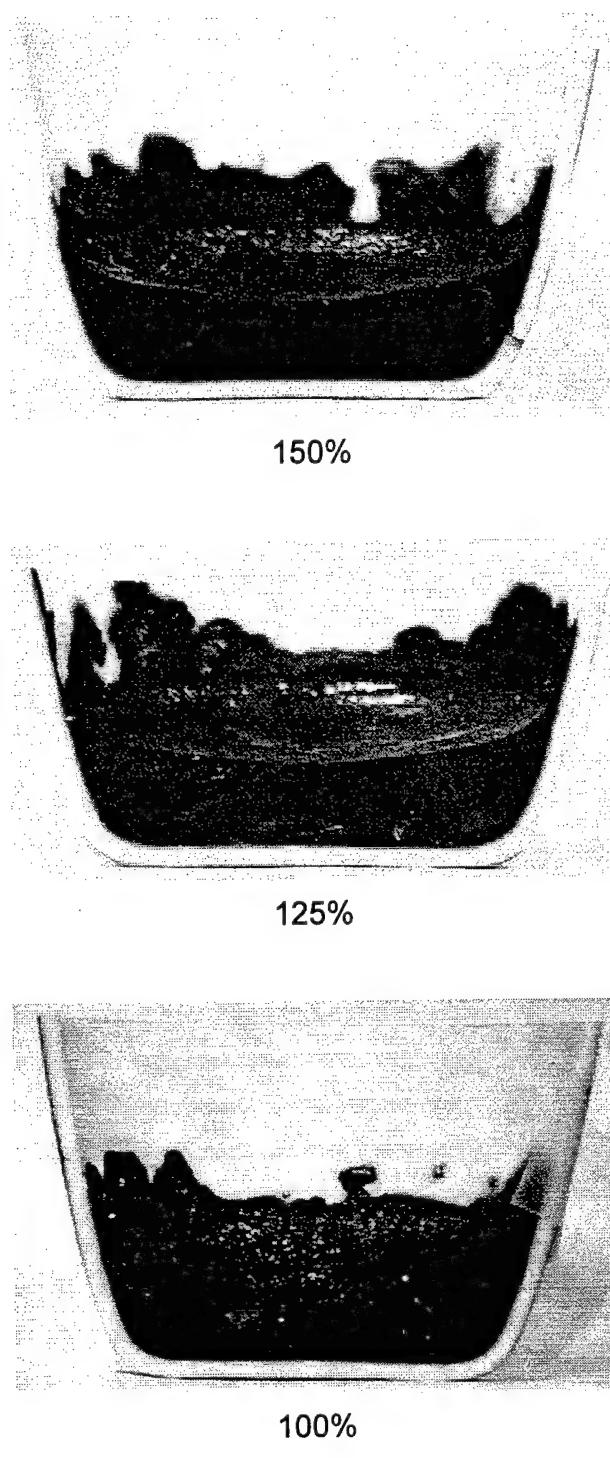
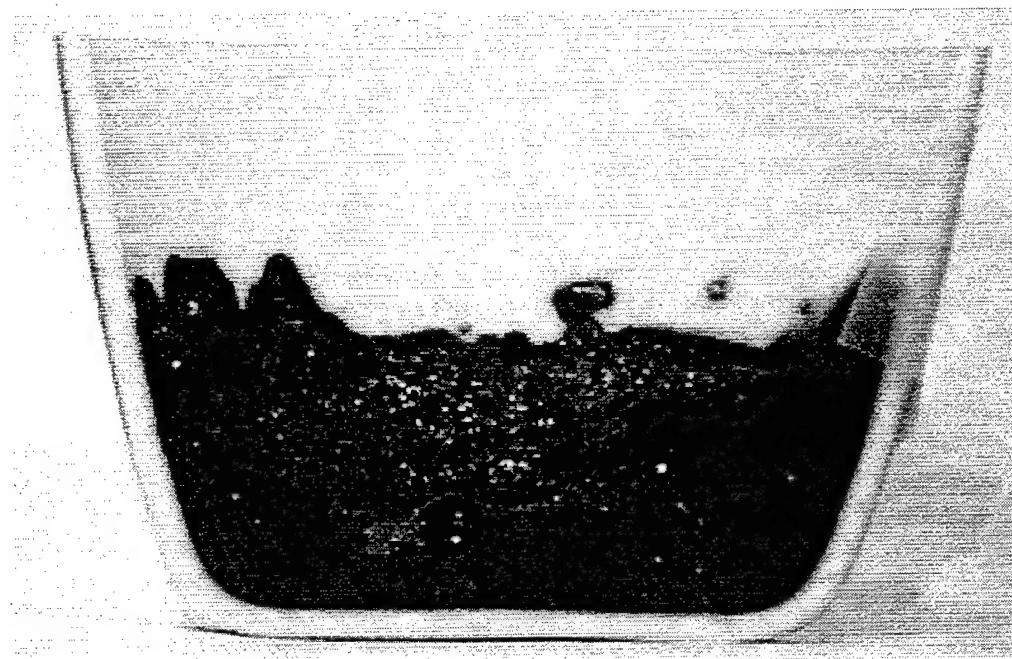
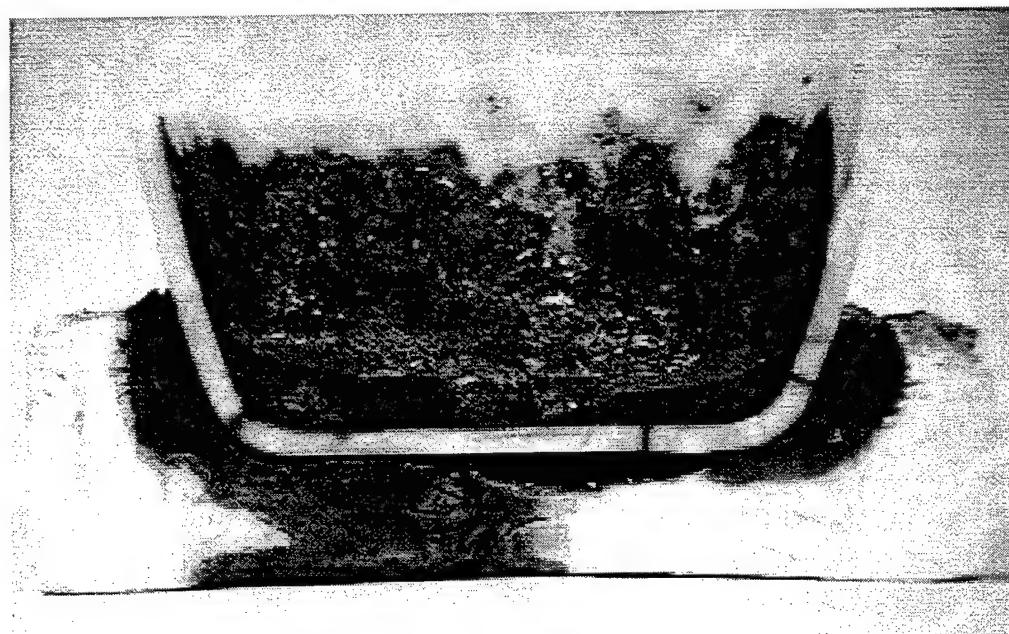


Figure 16. The Effect of Glass Excess on Melting Behavior of Slag (Values are in percent of glass in nominal slag which is 7.34%. Heating Conditions: 2-hour hold at 1400°C).

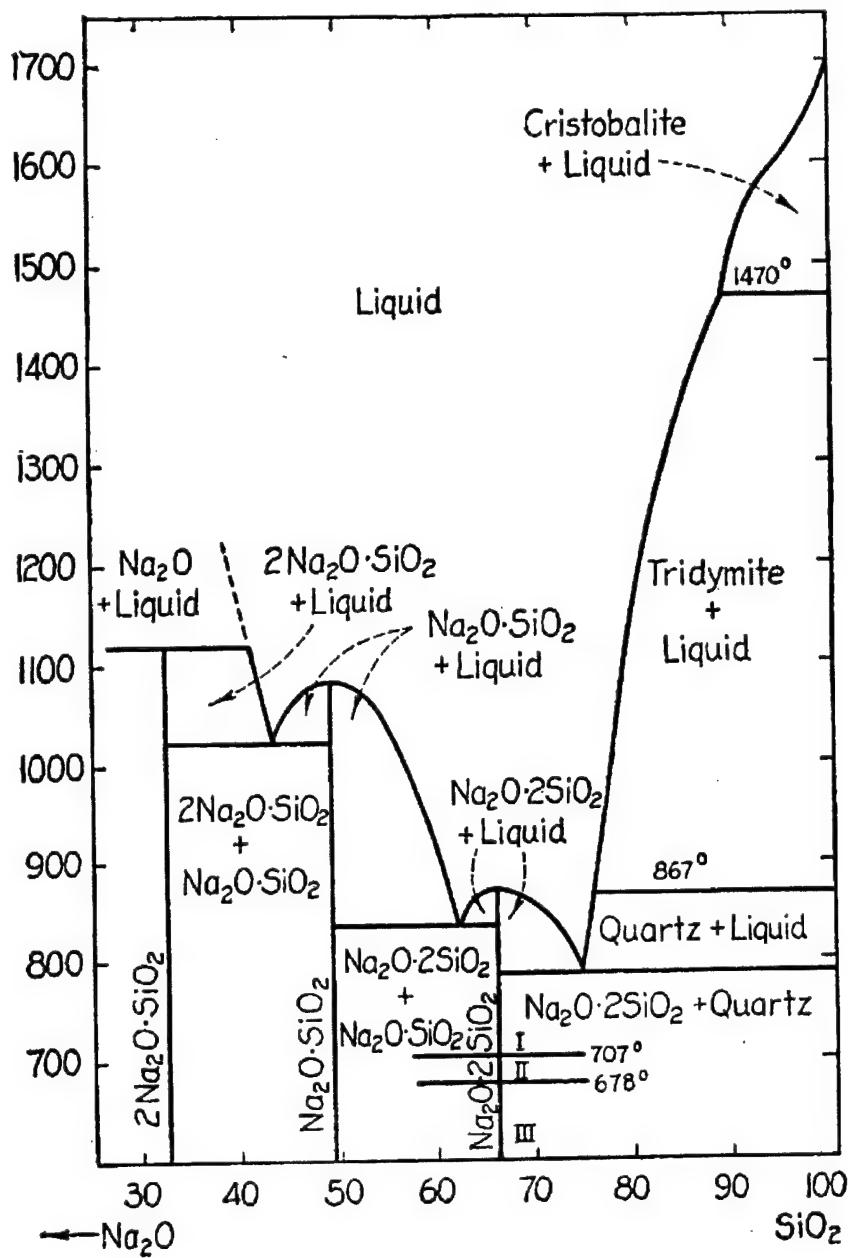


Nominal 1

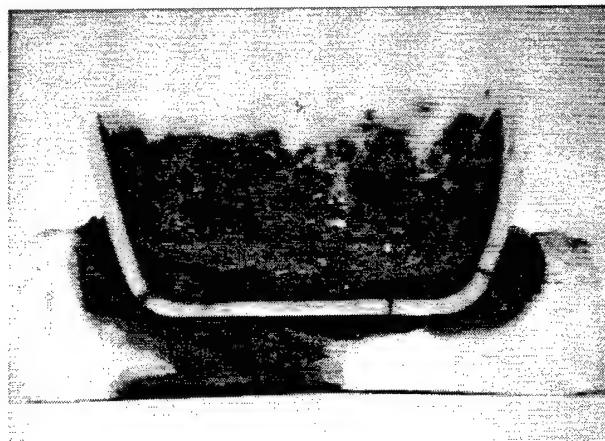


Sand replacing glass

Figure 17. Sand Substitution for Glass in Nominal 1 Slag (Heating Conditions: 4-hour hold at 1400°C).

$\text{Na}_2\text{O}-\text{SiO}_2$ Figure 18. System $\text{SiO}_2-2\text{Na}_2\text{O} \cdot \text{SiO}_2$.³

³ Levin, E.M., C.R. Robbins and H.F. McMurdie, editors. *Phase Diagrams for Ceramists*, Figure 192, The American Ceramic Society, Inc. 1964. F.C. Kracek, *J. Phys. Chem.*, 34, 1588, 1930. *J. Am. Chem. Soc.*, 61, 2869, 1939



Sand replaces glass



30% of 1:1 sand:Soda

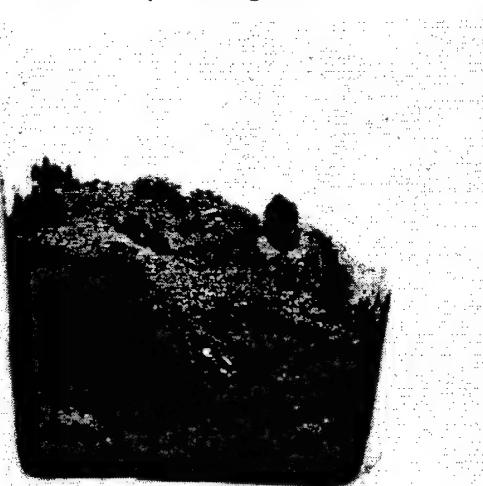


60% of 1:1 sand:Soda

Figure 19. Sand and Sand/Soda Substitution for Glass in Nominal 1 Slag (Heating Conditions: 2-hour hold at 1400°C).



Sand replaces glass

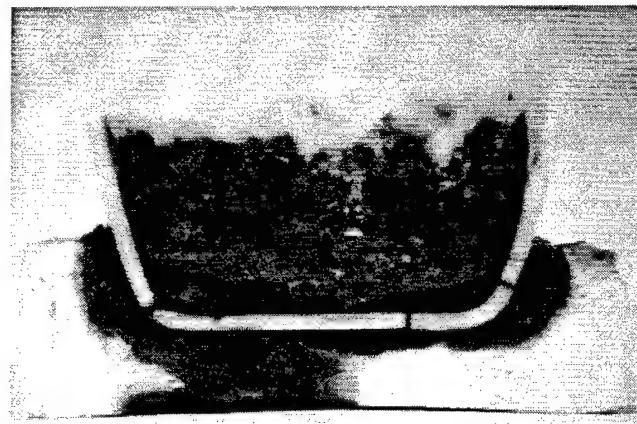


15% of 2:1 Sand:Soda



30% of 2:1 Sand:Soda

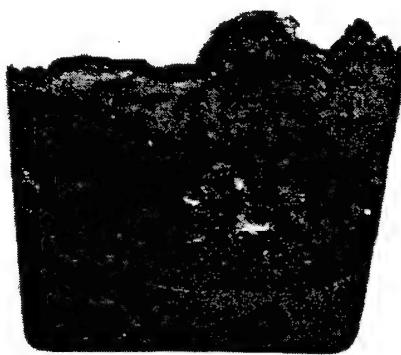
Figure 20. Sand and Sand/Soda Substitution for Glass in Nominal 1 Slag (Heating Conditions: 2-hour hold at 1400°C).



Sand replaces glass

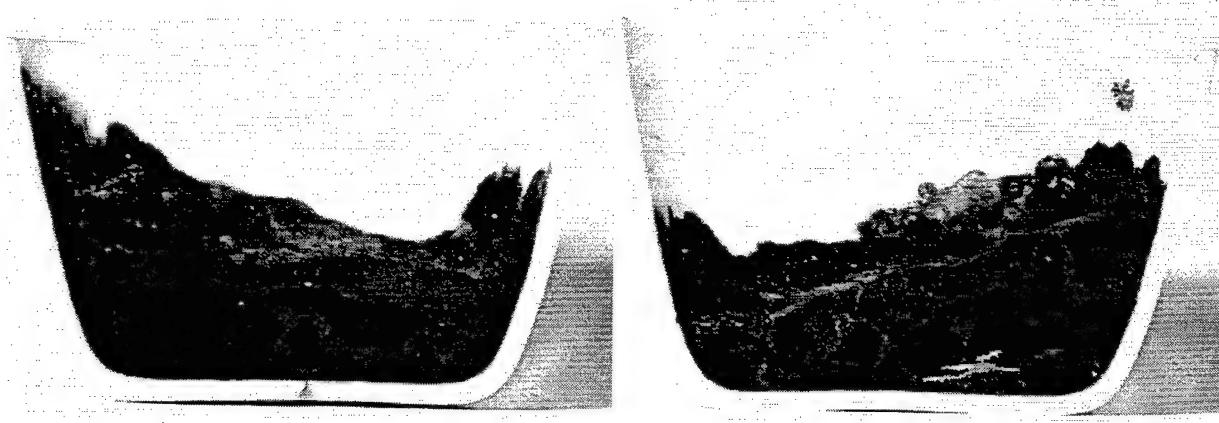


15% of 3:1 Sand:Soda



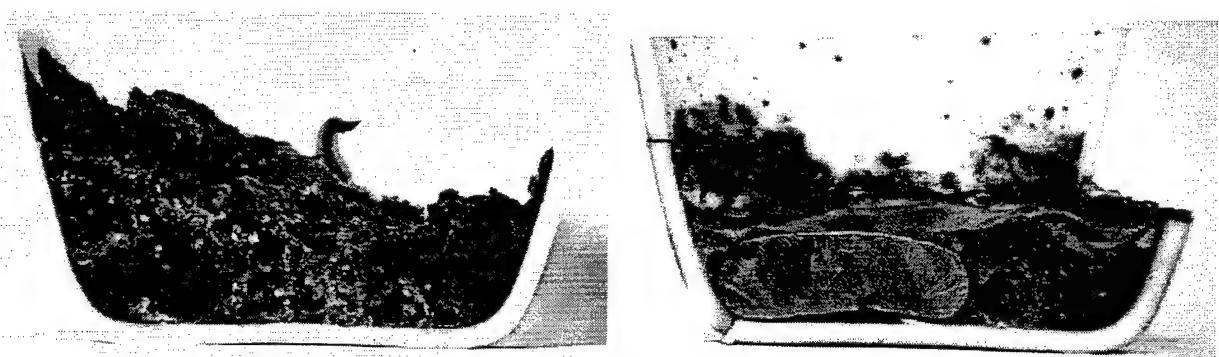
30% of 3:1 Sand:Soda

Figure 21. Sand and Sand/Soda Substitution for Glass in Nominal 1 Slag (Heating Conditions: 2-hour hold at 1400°C).



100% Substitution

60% Substitution



30% Substitution

15% Substitution

Figure 22. Waterglass Substitution for Glass in Nominal 1 Slag (Heating Conditions: 1400°C, 2-hour soak).

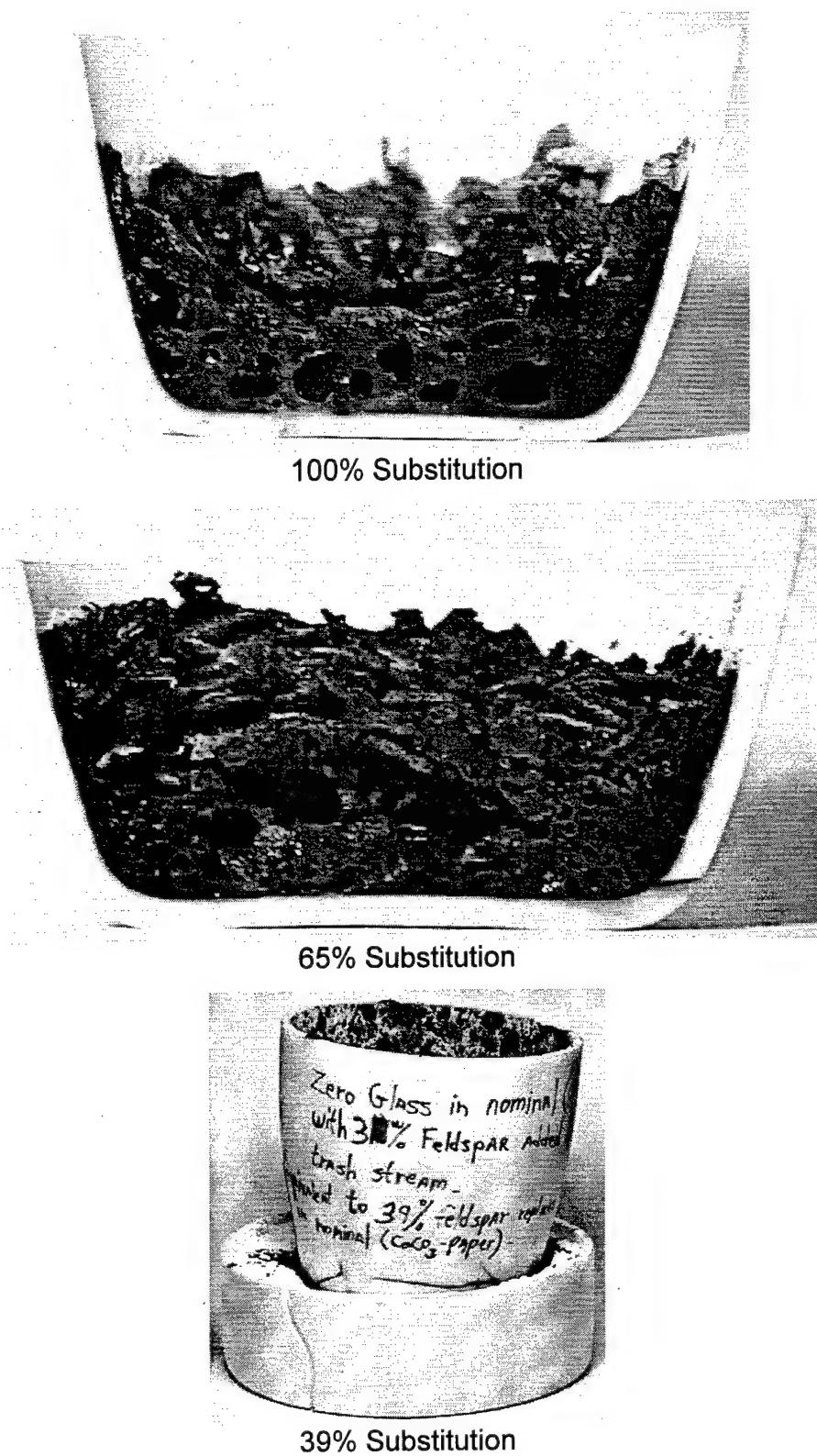


Figure 23. Feldspar Substitution for Glass in Nominal 1 Slag (Heating Conditions: 1400°C, 2-hour soak).

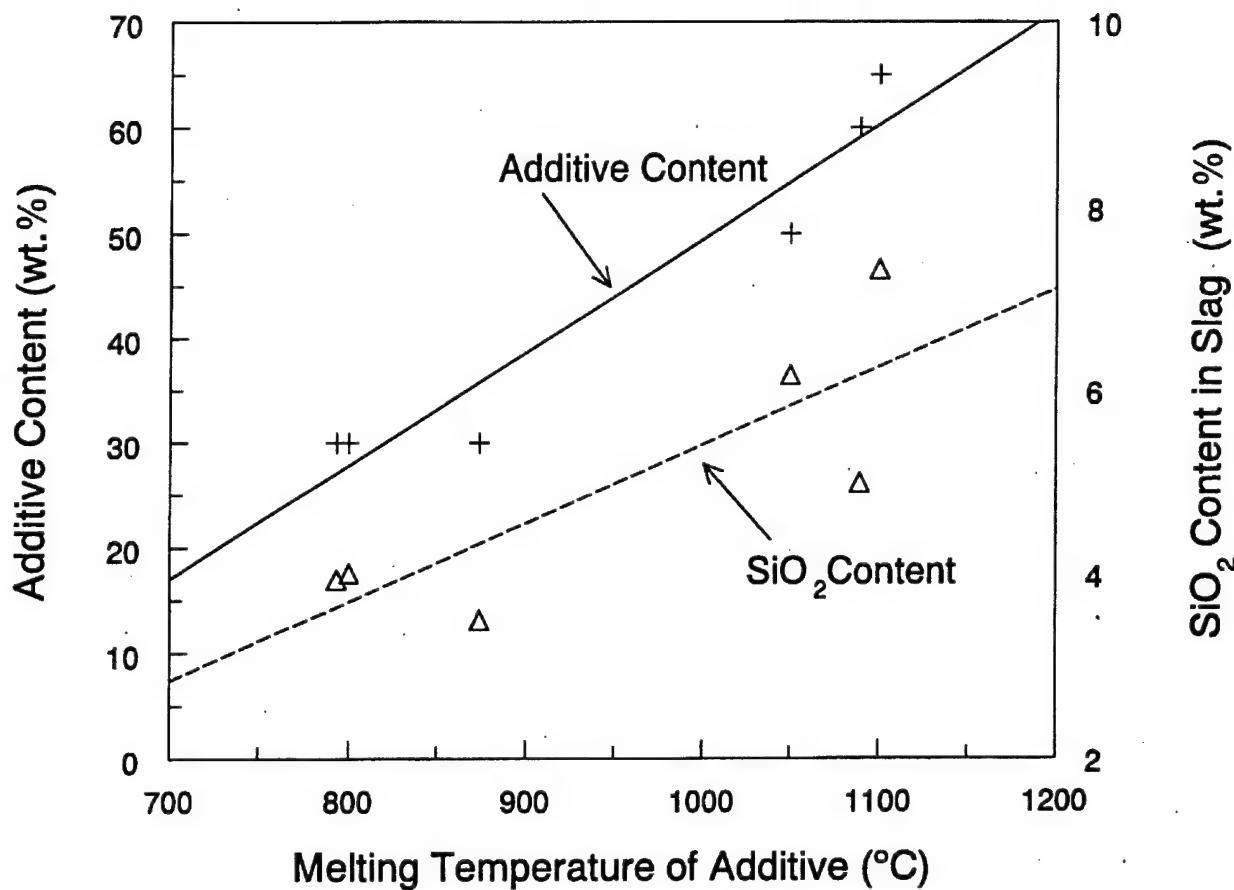


Figure 24. Effect of Flux Melting Temperature on Flux and Silica Content Required to Suppress Thermite Reaction.

Table 1. Waste Stream Variations.

Waste Components	Waste Stream Composition (weight %)					
	Nominal	Zero Food	Zero Paper	Zero Steel	Zero Aluminum	Zero Glass
Food	6.75	---	17.87	8.07	7.25	7.31
Paper	62.22	66.72	---	74.43	66.84	67.43
Steel	16.40	17.59	43.41	---	17.62	17.77
Aluminum	6.91	7.41	18.29	8.27	---	7.49
Glass	7.72	8.28	20.43	9.23	8.29	---
Total	100%	100%	100%	100%	100%	100%

Table 2. Predicted Chemical Composition of Slags Containing Different Types of Paper.

Oxides	Oxide Content in Various Slags (Weight %)		
	Nominal 1 with CaCO ₃	Nominal 2 with Kaolin	Nominal 3 With CaCO ₃ / Kaolin (50:50)
Fe ₃ O ₄	45.60	46.93	46.84
Al ₂ O ₃	26.49	31.40	29.77
SiO ₂	11.31	16.52	14.43
CaO	13.70	2.31	5.93
P ₂ O ₅	0.58	0.44	0.44
Na ₂ O	2.14	2.21	2.19

Table 3. Predicted Chemical Composition of Slags with CaCO_3 -Containing Paper.

Chemical Compounds	Oxide Content in Various Slags (weight %)				
	Nominal 1	Zero Paper	Zero Steel	Zero Aluminum	Zero Glass
Fe_3O_4	46.52	50.34	0	62.80	54.81
Al_2O_3	26.13	29.39	48.71	0.28	30.54
SiO_2	11.15	12.54	20.77	15.05	0
CaO	13.51	2.70	25.18	18.24	13.98
P_2O_5	0.57	0.64	1.06	0.76	0.67
Na_2O	2.11	2.38	3.94	2.86	0
K_2O	trace	trace	trace	0.06	0
MgO	0.12	0.14	0.23	0.17	0

Table 4. Results of Slag Simulation Experiments at 1400°C.

Waste Stream Variation	Metal Oxidation	Melting Behavior	Viscosity
Nominal 1	complete	complete melting and mixing	medium high
Zero Paper	no data	partial melting, poor mixing, metal chip morphology retained	not applicable
Zero Steel	no data	partial melting, metal chip morphology retained	not applicable
Zero Aluminum	complete	complete melting and mixing	very low
Zero Glass	almost complete (small amount of iron inclusions)	complete melting with splashing of melt and severe corrosion of crucible, some droplet-shape iron inclusions	very low

Table 5. Binary Oxide Ratios in Selected Slag Compositions.

(CaCO₃-containing paper)

Chemical Compounds	Binary Oxide Ratios in Various Slags (by weight)				
	Nominal 1 [melting]	Zero Paper [partial melting]	Zero Steel [partial melting]	Zero Aluminum [complete melting]	Zero Glass [splash melting]
Fe ₃ O ₄ /CaO	3.37	20.30	0/24.99	3.37	3.85
Al ₂ O ₃ /SiO ₂	2.34	2.34	2.34	0.02	31.20/0
SiO ₂ /CaO	0.84	5.04	0.84	0.84	0/14.07
Fe ₃ O ₄ /SiO ₂	4.03	4.03	0/20.9	4.04	54.19/0
Fe ₃ O ₄ /Al ₂ O ₃	1.72	1.72	0/49.01	207.00	1.74
Al ₂ O ₃ /CaO	1.96	11.80	1.96	0.02	2.21

Table 6. Chemical Composition of Slags with Variations in the Fe₃O₄ / CaO Ratio.

Chemical Compounds	Oxide Content (weight %) in Slags with Variations in the Fe ₃ O ₄ / CaO Ratio					
	0 (Zero Steel)	1	3.4 (Nominal)	9	15	20.3 (Zero Paper)
Fe ₃ O ₄	0	19.99	45.75	49.99	51.12	51.58
CaO	24.99	19.99	13.56	5.55	3.41	2.54
Al ₂ O ₃	49.01	39.19	26.57	29.03	29.70	29.96
SiO ₂	20.90	16.74	11.43	12.40	12.67	12.79
P ₂ O ₅	0.8	0.64	0.43	0.47	0.48	0.49
Na ₂ O	3.96	3.17	2.15	2.35	2.40	2.42
K ₂ O	trace	0.07	trace	trace	trace	trace
MgO	0.23	0.18	0.12	0.14	0.14	0.14

Table 7. The Effect of Fe_3O_4 / CaO Ratio on the Melting Behavior of Slags.

$\text{Fe}_3\text{O}_4/\text{CaO}$ Ratio for Waste Stream Variations	Metal Oxidation	Melting Behavior	Viscosity
0 (Zero Steel)	no data	partial melting, foaming, metal chip morphology retained,	not applicable
1	no data	complete melting and mixing	medium high
3.4 (Nominal)	complete	complete melting and mixing	medium high
9	incomplete (iron inclusions)	partial melting, poor mixing, metal chip morphology retained	not applicable
15	incomplete (iron inclusions)	partial melting, poor mixing, metal chip morphology retained	not applicable
20.3 (Zero Paper)	no data	partial melting, poor mixing, metal chip morphology retained	not applicable

Table 8. Waste Stream Composition for Variations in Glass Content.

Waste Components	Waste Stream Composition (weight %) for Variations in Glass Content					
	0% (Zero Glass)	15%	18%	30%	50%	100% (Nominal)
Steel	17.77	17.55	17.51	17.34	17.06	16.4
Paper	67.43	66.59	66.43	65.77	64.71	62.22
Aluminum	7.49	7.39	7.38	7.31	7.19	6.91
Glass	---	1.24	1.47	2.45	4.02	7.72
Food	7.31	7.22	7.21	7.14	7.02	6.75

Table 9. Chemical Composition of Slags with Variations in Glass Content.

Oxide	Oxide Content (weight %) in Slags with Variations in Glass					
	0 (Zero Glass)	15%	18%	30%	50%	100% (Nominal)
Fe ₃ O ₄	53.98	52.74	52.47	51.35	49.61	45.60
CaO	14.24	13.98	13.96	13.89	13.79	13.70
Al ₂ O ₃	31.11	30.42	30.27	29.66	28.70	26.49
SiO ₂	---	1.96	2.33	3.82	6.17	11.31
P ₂ O ₅	0.68	0.50	0.50	0.49	0.47	0.58
Na ₂ O	---	0.37	0.44	0.72	1.17	2.14
K ₂ O	---	trace	trace	trace	trace	trace

Table 10. Waste Composition with Variations in Glass Content.

Waste Components	Waste Stream Composition (weight %) for Variations in Glass Content						
	0% (Zero Glass)	15%	30%	50%	100% (Nominal)	125%	150%
Steel	17.77	17.55	17.34	17.06	16.4	16.09	15.79
Paper	67.43	66.59	65.77	64.71	62.22	61.04	59.90
Aluminum	7.49	7.39	7.31	7.19	6.91	6.77	6.65
Glass	---	1.24	2.45	4.02	7.72	9.46	11.15
Food	7.31	7.22	7.14	7.02	6.75	6.62	6.50

Table 11. Chemical Composition of Slags with Variations in Glass Content.

Oxide	Oxide Content (weight %) in Slags with Variations in Glass						
	0 (Zero Glass)	15%	30%	50%	100% (Nom- inal)	125%	150%
Fe ₃ O ₄	53.98	52.74	51.35	49.61	45.60	44.03	42.44
CaO	14.24	13.98	13.89	13.79	13.70	13.45	13.36
Al ₂ O ₃	31.11	30.42	29.66	28.70	26.49	25.63	24.75
SiO ₂	---	1.96	3.82	6.17	11.31	13.65	15.79
P ₂ O ₅	0.68	0.50	0.49	0.47	0.58	0.42	0.40
Na ₂ O	---	0.37	0.72	1.17	2.14	2.59	2.99
K ₂ O	---	trace	trace	trace	trace	trace	trace
MgO	---	trace	trace	trace	0.12	0.15	0.17

Table 12. Results of Simulation Experiments on Slags with Various Glass Content.

Waste Stream Variation, % Glass	Heating Temp. (°C)	Melting Behavior
0 (Zero Glass)	1400	complete melting, severe thermite reaction and corrosion of crucible , secondary iron present
15	1400	complete melting, severe thermite reaction and corrosion of crucible , secondary iron present
30	1400	complete melting, thermite reaction, severe cracking of crucible , secondary iron present
50	1400	complete melting, very weak thermite reaction, no corrosion of crucible , some secondary iron present
100 (Nominal)	1400	complete melting, weak thermite reaction is possible, no corrosion of crucible , occasional presence secondary iron present
125	1400	complete melting, no thermite reaction , no secondary iron present
150	1400	complete melting, no thermite reaction , no secondary iron present

Table 13. Chemical Composition of Slags with Variations in Sand / NaHCO₃ Content
(SiO₂/Na₂O ratio 1:1) Introduced as Substitution for Glass.

Oxide	Oxide Content (weight %) in Slags			
	0 (Zero Glass)	30% Sand/NaHCO ₃	60% Sand/NaHCO ₃	100% (Nominal)
1400°C, 2hr	Thermite	Thermite	No thermite	No thermite
Fe ₃ O ₄	53.98	51.32	48.76	45.60
CaO	14.24	13.34	12.67	13.70
Al ₂ O ₃	31.11	29.60	28.12	26.49
SiO ₂	---	2.63	4.99	11.31
Na ₂ O	---	2.63	4.99	2.14
P ₂ O ₅	0.68	0.49	0.46	0.58

Table 14. Chemical Composition of Slags with Variations in Sand / NaHCO₃ Content
(SiO₂/Na₂O ratio 2:1) Introduced as Substitution for Glass.

Oxide	Oxide Content (weight %) in Slags				
	0 (Zero Glass)	15% Sand/ NaHCO ₃	30% Sand/ NaHCO ₃	60% Sand/ NaHCO ₃	100% (Nominal)
1400°C, 2hr	Thermite	Thermite	No thermite	No thermite	No thermite
Fe ₃ O ₄	53.98	52.71	51.32	48.76	45.60
CaO	14.24	13.70	13.34	12.67	13.70
Al ₂ O ₃	31.11	30.40	29.60	28.12	26.49
SiO ₂	---	1.80	3.5	6.65	11.31
Na ₂ O	---	0.90	1.75	3.33	2.14
P ₂ O ₅	0.68	0.50	0.49	0.46	0.58

Table 15. Chemical Composition of Slags with Variations in Sand / NaHCO₃ Content (SiO₂/Na₂O ratio 3:1) Introduced as Substitution for Glass.

Oxide	Oxide Content (weight %) in Slags			
	0 (Zero Glass)	15% Sand /NaHCO ₃	30% Sand /NaHCO ₃	100% (Nominal)
1400°C, 2hr	Thermite	Thermite	No thermite	No thermite
Fe ₃ O ₄	53.98	52.71	51.32	45.60
CaO	14.24	13.7	13.34	13.70
Al ₂ O ₃	31.11	30.40	29.60	26.49
SiO ₂	---	2.02	3.94	11.31
Na ₂ O	---	0.67	1.31	2.14
P ₂ O ₅	0.68	0.50	0.49	0.58

Table 16. Development of Thermite Reaction in Nominal Slags as a Function of Chemical and Physical Transformations of the Components during Heating.

Nominal with glass	Nominal with sand	Nominal with sand + Na ₂ O (NaHCO ₃) 2:1 ratio
660°C, Al melts	660°C, Al melts	660°C, Al melts
1050°C, glass melts	Sand doesn't melt (T _{mp} ~1700°C)	~874°C eutectic in the SiO ₂ - Na ₂ O system
Al oxidized by redox reaction with SiO ₂	Redox reaction inefficient in solid state	Al oxidized by redox reaction with SiO ₂
1000°C, Fe oxidizes		
1200°C, thermite reaction ignition temperature		
Weak thermite reaction	Severe thermite reaction	No thermite reaction

Table 17. Chemical Composition of Slags with Variations in Sodium Silicate Content.

Oxide	Oxide Content (weight %) in Slags with Variations in $\text{Na}_2\text{O}/3.22\text{SiO}_2$ Content				
	0 (Zero Glass)	(15% of glass)	(30% of glass)	(60% of glass)	(100% of glass)
1400°C, 2 hr	Thermite	Thermite	No thermite	No thermite	No thermite
Fe_3O_4	53.98	52.72	51.32	48.76	45.76
CaO	14.24	13.70	13.34	12.67	11.87
Al_2O_3	31.11	30.40	29.60	28.12	26.34
SiO_2	---	2.05	4.01	7.61	11.90
P_2O_5	0.68	0.50	0.49	0.46	0.43
Na_2O	---	0.63	1.24	2.36	3.70

Table 18. Chemical Composition of Slags with Variations in Feldspar Content.

Oxide	Oxide Content (weight %) in Slags with Variations in Feldspar Content				
	0 (Zero Glass)	(40% of glass)	(65% of glass)	(100% of glass)	100% (Nominal)
1400°C, 2 hr	Thermite	Thermite	No thermite	No thermite	No thermite
Fe_3O_4	53.98	50.85	48.40	45.80	45.60
CaO	14.24	13.29	12.73	12.12	13.70
Al_2O_3	31.11	30.43	29.87	29.23	26.49
SiO_2	---	4.26	7.33	10.70	11.31
P_2O_5	0.68	0.48	0.46	0.44	0.58
Na_2O	---	0.43	0.74	1.07	2.14
K_2O	---	0.25	0.44	0.64	trace
MgO	---	trace	trace	trace	0.12

Table 19. Chemical Composition of Slags with Variations in Na₂O Content.

Oxide	Oxide Content (weight %) in Slags with Variations in Na ₂ O Content				
	(Zero Glass)	(13% of glass)	(40% of glass)	(60% of glass)	(Nominal 1)
1400°C, 2 hr	Thermite	Thermite	Thermite	No thermite	No thermite
Fe ₃ O ₄	53.98	52.87	55.40	48.76	45.60
CaO	14.24	13.74	13.13	12.67	13.70
Al ₂ O ₃	31.11	30.50	29.15	28.12	26.49
SiO ₂	0.00	0.00	0.00	0.00	11.31
P ₂ O ₅	0.68	0.50	0.48	0.46	0.58
Na ₂ O	trace	2.38	6.70	9.98	2.14

Table 20. Effect of the Silicon Oxide Content and Flux Melting Temperature in Various Slags on the Development of Thermite Reaction.

Flux Composition and Amount	Flux Melting Temperature, °C	SiO ₂ Content, %	Thermite Reaction?
Glass Series			
Nominal 1	1050	11.3	no
30% glass		3.8	yes
50% glass		6.2	no
Feldspar Series			
40% of glass	1100	4.3	yes
65% of glass		7.3	no
Water Glass Series (SiO₂/Na₂O ratio = 3.22:1)			
15% of glass	800	2.0	yes
30% of glass		4.0	no
Sand+Soda Series			
SiO ₂ / Na ₂ O ratio=1:1	1089		
30% of glass		2.6	yes
60% of glass		5.0	no
SiO ₂ / Na ₂ O ratio=2:1	874		
15% of glass		1.8	yes
30% of glass		3.5	no
SiO ₂ / Na ₂ O ratio=3:1	793		
15% of glass		2.0	yes
30% of glass		3.9	no

Table 21. Effect of the Silicon Oxide/Aluminum Ratios in Various Slags on the Development of Thermite Reaction.

Flux Composition and Amount	SiO ₂ /Al ratio	Thermite Reaction?
Glass Series		
Nominal 1	0.806	no
30% glass	0.243	yes
50% glass	0.406	no
Feldspar Series		
40% of glass	0.264	yes
65% of glass	0.463	no
Water Glass Series (SiO ₂ /Na ₂ O ratio = 3.22:1)		
15% of glass	0.127	yes
30% of glass	0.256	no
Sand+Soda Series		
SiO ₂ / Na ₂ O ratio=1:1		
30% of glass	0.168	yes
60% of glass	0.335	no
SiO ₂ / Na ₂ O ratio=2:1		
15% of glass	0.112	yes
30% of glass	0.223	no
SiO ₂ / Na ₂ O ratio=3:1		
15% of glass	0.126	yes
30% of glass	0.251	no

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